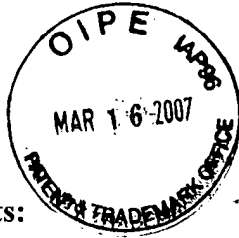


03-19-07

ITJ

PATENT



Publication No. US 2007/0043168 A1

Applicants: Montiel-Ortiz, et al.

Application No.: 10/560,929

Publication No.: US 2007/0043168 A1

Filing/371 Date: September 25, 2006

Publication Date: February 22, 2007

Title: RANDOM COPOLYMER TO MANUFACTURE  
TRANSPARENT EXTRUDED PRODUCTS

Group Art Unit: 1713

Examiner: Reddy, K. P.

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GREGORY MILLS  
QUALITY ASSURANCE SPECIALIST

**THIRD-PARTY SUBMISSION OF PRIOR ART  
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To Whom It May Concern:

Pursuant to 37 C.F.R. § 1.99, a member of the public hereby submits the following patents or publications for consideration by the Office:

1. U.S. Patent No. 4,386,190, issued May 31, 1983;
2. U.S. Patent No. 5,587,425, issued December 24, 1996;
3. U.S. Patent No. 6,107,411, issued August 22, 2000;
4. U.S. Patent No. 6,841,261, issued January 11, 2005; and
5. U.S. Publication No. US 2007/0027257, published February 1, 2007.

The U.S. Patent and Trademark Office (PTO) is hereby authorized to charge the appropriate fee under 37 C.F.R. § 1.17(p) for this submission.

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Rick J. Moss

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In accordance with 37 C.F.R. § 1.99(e), this submission is being filed within two months from the date of publication of the application.

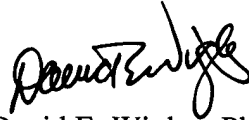
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Respectfully submitted,



David E. Wigley, Ph.D.  
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Date: March 16, 2007  
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PATENT



Publication No. US 2007/0043168 A1

**Applicants:** Montiel-Ortiz, et al

**Application No.:** 10/560,929

**Publication No.:** US 2007/0043168 A1

**Filing/371 Date:** September 25, 2006

**Publication Date:** February 22, 2007

**Title:** RANDOM COPOLYMER TO MANUFACTURE  
TRANSPARENT EXTRUDED PRODUCTS

**Group Art Unit:** 1713

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**Examiner:** Reddy, K. P.

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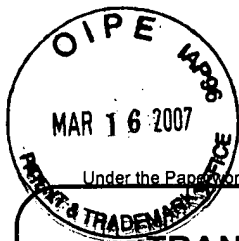
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**TRANSMITTAL  
FORM**

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Total Number of Pages in This Submission

75

Application Number

10/560,929

Filing Date

September 25, 2006

First Named Inventor

Leobardo Montiel-Ortiz

Art Unit

1713

Examiner Name

Reddy, K. P.

Attorney Docket Number

N/A

**ENCLOSURES (Check all that apply)**

Fee Transmittal Form



Fee Attached



Amendment/Reply



After Final



Affidavits/declaration(s)



Extension of Time Request



Express Abandonment Request



Information Disclosure Statement



Certified Copy of Priority Document(s)

Reply to Missing Parts/  
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Drawing(s)



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Petition

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Date

March 16, 2007

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52,362

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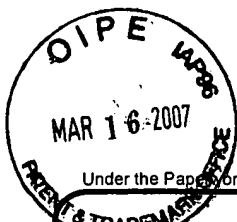
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# FEE TRANSMITTAL

## For FY 2006

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$) 180.00

### Complete if Known

Application Number	10/560,929
Filing Date	September 25, 2006
First Named Inventor	Leobardo Montiel-Ortiz
Examiner Name	Reddy, K. P.
Art Unit	1713
Attorney Docket No.	N/A

### METHOD OF PAYMENT (check all that apply)

☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): \_\_\_\_\_

☒ Deposit Account Deposit Account Number: 13-2725 Deposit Account Name: Merchant & Gould, LLC

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### FEE CALCULATION

#### 1. BASIC FILING, SEARCH, AND EXAMINATION FEES

Application Type	FILING FEES		SEARCH FEES		EXAMINATION FEES		Fees Paid (\$)
	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	
Utility	300	150	500	250	200	100	-
Design	200	100	100	50	130	65	-
Plant	200	100	300	150	160	80	-
Reissue	300	150	500	250	600	300	-
Provisional	200	100	0	0	0	0	-

#### 2. EXCESS CLAIM FEES

Fee Description	Fee (\$)	Small Entity Fee (\$)
Each claim over 20 (including Reissues)	50	25
Each independent claim over 3 (including Reissues)	200	100
Multiple dependent claims	360	180
Total Claims		
- 20 or HP =	x	=
HP = highest number of total claims paid for, if greater than 20.		
Indep. Claims		
- 3 or HP =	x	=
HP = highest number of independent claims paid for, if greater than 3.		

#### 3. APPLICATION SIZE FEE

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$250 (\$125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

Total Sheets	Extra Sheets	Number of each additional 50 or fraction thereof	Fee (\$)	Fee Paid (\$)
- 100 =	/ 50 =	(round up to a whole number) x	-	-

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Non-English Specification, \$130 fee (no small entity discount)	Fees Paid (\$)
Other (e.g., late filing surcharge): Fee for Third-Party Submission of Prior Art	180.00

### SUBMITTED BY

Signature	<u>David E. Wigley</u>	Registration No. (Attorney/Agent)	52,362	Telephone	404-954-5056
Name (Print/Type)	David E. Wigley, Ph.D.			Date	March 16, 2007

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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# United States Patent [19]

Bailey

[11] 4,386,190

[45] May 31, 1983

[54] POLYMER BLEND OF DIENE/VINYL  
AROMATIC BLOCK COPOLYMER AND  
STYRENE/ACRYLATE COPOLYMER

[75] Inventor: Fay W. Bailey, Bartlesville, Okla.

[73] Assignee: Phillips Petroleum Company,  
Bartlesville, Okla.

[21] Appl. No.: 410,767

[22] Filed: Aug. 23, 1982

[51] Int. Cl.<sup>3</sup> ..... C08L 53/02

[52] U.S. Cl. .... 525/93; 525/901;  
525/96

[58] Field of Search ..... 525/96, 901, 93

## [56] References Cited

### U.S. PATENT DOCUMENTS

3,261,887	7/1966	Mann .....	260/876
3,300,545	1/1967	Baer .....	260/876
3,919,157	11/1975	Ide et al. ....	260/29.7 T
3,950,292	4/1976	Cooper .....	260/23.7
4,100,228	7/1978	Dennis et al. ....	260/880
4,104,326	8/1978	Fodor .....	260/876 B
4,117,035	9/1978	Hillier et al. ....	525/901
4,160,001	7/1979	Rosen .....	525/230
4,195,136	3/1980	Sato et al. ....	525/71

Primary Examiner—Carman J. Seccuro

## [57] ABSTRACT

A high impact resistant polymer is provided comprising a blend of (a) a resinous, essentially non-elastomeric copolymer of a conjugated diene and vinylarene and (b) a copolymer of a vinylarene and an acrylate.

5 Claims, No Drawings

# **POLYMER BLEND OF DIENE/VINYL AROMATIC BLOCK COPOLYMER AND STYRENE/ACRYLATE COPOLYMER**

This invention relates to durable high impact resistant polymer blends. More specifically, this invention relates to blends of (a) resinous, essentially non-elastomeric copolymers of conjugated dienes and vinylarenes and (b) copolymers of vinylarenes and acrylates.

The existence of impact resistant copolymers of conjugated dienes and vinylarenes is known in the art as disclosed in U.S. Pat. No. 4,104,316 and U.S. Pat. No. 4,195,136. In addition, it is known that blends of the abovedescribed copolymers and copolymers of vinylarenes and acrylates result in impact resistant polymers.

These polymer blends have important applications as ingredients in molded articles of manufacture, particularly in food containers. Because the food containers are frequently packaged as part of large bundles and sometimes shipped long distances, they are highly susceptible to damage resulting in loss of the food product. Therefore, polymer blends which exhibit an even higher impact resistance than heretofore exhibited by similar ones are highly desirable because of their durability.

Therefore, an object of this invention is to provide a polymer blend of improved high impact resistance. A further object is to provide an improved high impact resistant polymer blend of (a) copolymers of conjugated dienes and vinylarenes and (b) copolymers of vinylarenes and acrylates.

Other aspects, objects, and advantages of this invention will become apparent from a study of this specification and the appended claims.

In accordance with the present invention, I have discovered a polymeric compositions of improved high impact resistance which comprises a blend of (a) resinous, essentially non-elastomeric copolymers of conjugated dienes and vinylarenes, and (b) copolymers of vinylarenes and acrylates. Preferably, (a) is a block copolymer of conjugated dienes and vinylarenes.

More specifically, in accordance with the present invention, I have discovered an improved high impact resistant polymeric compositions which comprises a blend of (a) a copolymer consisting of from about 64-70 weight percent of a vinylarene and from about 30-36 weight percent of a conjugated diene and (b) a copolymer consisting of a vinylarene and an acrylate, said blend having a total conjugated diene content of from about 21 to about 34 weight percent.

In a preferred embodiment, the blend will have a total conjugated diene content of from 32 to 34 weight percent. It is generally preferred to use conjugated diene-monomovinylarene copolymers prepared by employing an alkali-metal-based initiator to copolymerize the monomers in a hydrocarbon diluent. The conjugated dienes generally preferred in the copolymerization are those of 4 to 12 carbon atoms per molecule with those of 4-8 carbon atoms per molecule being more preferred. Examples of these monomers include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, piperylene, 3-butyl-1,3-octadiene and 2-phenyl-1,3-butadiene. The generally preferred vinylarenes contain 8-20, and more preferably 8-12, carbon atoms per molecule. Examples include styrene, alpha-methylstyrene, 1-vinylnaphthalene, 2-vinylnaphthalene and alkyl, cycloalkyl, aryl, alkaryl and aralkyl derivatives thereof. Examples of substituted monomers include 3-methylstyrene, 4-n-pro-

pylstyrene, 4-cyclohexylstyrene, 4-dodecylstyrene, 3-ethyl-4-benzylstyrene, 4-p-tolylstyrene and 4-(4-phenyl-n-butyl)styrene.

The vinylarene-acrylate copolymers of my inventive blends can be prepared by copolymerizing at least one vinylarene (as described above) such as styrene, alpha-methylstyrene, o-, m- or p-vinyltoluene, 2,4-dimethylstyrene, 2,4-diethylstyrene, 2-chlorostyrene, 2-chloro-5-methylstyrene, vinylnaphthalene and the like, or mixtures thereof, with at least one substituted or unsubstituted alkyl acrylate, such as methylacrylate, ethylacrylate, isopropylacrylate, butylacrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, methyl ethacrylate, and the like, or mixtures thereof.

The preferred vinylarene-acrylate copolymer to be used in my inventive blends is a styrene-methyl methacrylate copolymer.

My inventive blends can be prepared by any suitable mixing means, such as dry-blending, melt-blending and solution-blending. The preferred mode of operation is by dry-blending of the components, e.g., in a drum tumbler, for obtaining blends of maximum impact resistance.

In molded objects prepared by any of the well known molding techniques, preferably by injection molding, my inventive blends show a surprisingly high Gardner impact resistance.

The following examples are intended to further illustrate my invention. However, particular materials, ratios and procedures should be considered exemplary and not limitative of the reasonable scope of this invention.

## **EXAMPLE I**

In this example, the preparation of a resinous, polymodal, radially branched butadiene-styrene copolymer is described. This copolymer was prepared in a developmental K-Resin® pilot plant of Phillips Petroleum Company, and it was used later for preparing my inventive blends.

400 lb. of cyclohexane and 0.05 lb. of tetrahydrofuran were charged to an agitated reactor. Then 0.06 lb. of n-butyllithium initiator was added, followed by the first styrene charge of 59 lb. The temperature was raised from about 50° C. to about 80° C. during a time period of about 4 minutes after the styrene charge. The second styrene portion of 33 lb. was added after briefly cooling the reactor about 20° C. below the previous peak temperature and reheating to about 80° C., which occurred about 21 minutes after the first styrene charge. The third portion of styrene (40 lb.) and the second n-butyllithium charge (0.32 lb) followed after a brief cooling down period. A third peak temperature of about 87° C. was reached 32 minutes after the first styrene charge. The reactor pressure during these three reaction stages was about 21-24 psig. Finally, about 50 minutes after the start of the polymerization reaction, 68 lb. of butadiene were added. The temperature was raised to about 100° C., and the pressure was raised to about 45 psig, during a period of about 5 minutes. Then 1.0 lb. of Admex 711, an epoxidized soybean oil coupling agent marketed by Sherex Chemical Company, was added.

The copolymer solution was transferred to a blow-down vessel to which 0.8 lb. of water plus 0.8 lb. of CO<sub>2</sub> were charged as terminating agents. Then 1.9 lb of BHT (2,6-di-t-butyl-p-cresol) and 1.3 lb of TNPP (tris-nonyltriphenyl phosphite) were added as antioxidants,

and 0.5 lb of a microcrystalline paraffin wax was added as an antiblocking agent. Finally, the copolymer was recovered by solvent removal in a film evaporator and a devolatilizing extruder. The polymer melt flow at 200° C. of the prepared resinous, polymodal, branched copolymer having a weight ratio of butadiene:styrene of 34:66 was 7.0 g/10 minutes at 200° C. (ASTM D1238, Condition G). Another copolymer having a 32:68 butadiene:styrene weight ratio and having a melt flow of 6.8 g/10 minutes was prepared by essentially the same polymerization procedure as described earlier in this example.

### EXAMPLE II

Pellets of the resinous, polymodal butadiene-styrene copolymers of Example I having a bound styrene content of 66-68 weight percent were dry-blended by tumbling in a plastic bag with various amounts of pelletized Noan 80, a styrene-methyl methacrylate copolymer having a bound styrene content of 80 weight percent, a melt flow of about 2.0 g/10 min. (ASTM D1238 Condition G), a specific gravity of 1.08, and a deflection temperature (annealed, ASTM D648) of 99° C., marketed by Richardson Company, Madison, Conn., under the tradename of Noan 80. The dry-blending was done manually for about 60 seconds.

Prepared blends were molded in an Arburg 221 E/150 1½ ounce molding machine at a barrel temperature of about 200° C., a mold temperature of 50° C., a screw speed of 120 r.p.m., and an injection pressure of about 63-75 MPa. Total cycle time was about 35 minutes. Molded disks of an average thickness of 57 units (1.45 mm) made of various inventive and control blends containing resinous butadiene-styrene copolymer and styrene-methyl methacrylate copolymer were tested in a Gardner IG-1120 heavy-duty impact tester according to a modified ASTM D2444-70 procedure described in the IG-1120 manual of Gardner Laboratories, Bethesda, Md. All tests were carried out with a 4-lb weight and a 40 inch guide tube slot at room temperature for determining impact energy which divided by the specimen thickness in millimeters to give impact values in units of an Kg/mm<sup>2</sup>. Impact data are listed in Table I.

TABLE I

Run	Weight-% of K-Resin® <sup>(1)</sup>	Weight-% of Noan 80 <sup>(2)</sup>	Weight-% Butadiene in Blend <sup>(3)</sup>	Gardner Impact <sup>(4)</sup> (cm · kg/mm)
1 (Control)	100	0	34.0	56
2 (Control)	100	0	32.0	61
3 (Invention)	93.7	6.3	30.0	66
4 (Invention)	85.9	14.1	27.5	69
5 (Invention)	85.0	15.0	28.9	58 <sup>(5)</sup>
6 (Invention)	78.1	21.9	25.0	77
7 (Invention)	75.0	25.0	25.5	66
8 (Invention)	70.3	29.7	22.5	74
9 (Control)	62.5	37.5	20.0	62
10 (Control)	55.0	45.0	18.7	43
11 (Control)	50.0	50.0	17.0	57
12 (Control)	45.0	55.0	15.3	43

TABLE I-continued

Run	Weight-% of K-Resin® <sup>(1)</sup>	Weight-% of Noan 80 <sup>(2)</sup>	Weight-% Butadiene in Blend <sup>(3)</sup>	Gardner Impact <sup>(4)</sup> (cm · kg/mm)
13 (Control)	39.1	60.9	12.5	0.5
14 (Control)	35.0	65.0	11.9	58 <sup>(5)</sup>
15 (Control)	25.0	75.0	8.5	less than 1
16 (Control)	0	100	0	less than 1

<sup>(1)</sup>an experimental resinous, polymodal, radial butadiene-styrene copolymer having bound butadiene content of 32-34 weight percent and a bound styrene content of 68-66 weight percent.

<sup>(2)</sup>a styrene-methyl methacrylate copolymer having a bound styrene content of 80 weight percent marketed by Richardson Company;

<sup>(3)</sup>

$\frac{\text{weight-\% K-Resin® in blend}}{100} \times \text{weight-\% bound butadiene in K-Resin®}$

<sup>(4)</sup>determined according to the modified ASTM D2444-70 procedure described in Gardner Laboratories IG-1120 manual, using a 4 lb weight;

<sup>(5)</sup>most likely erroneous results.

Data in Table I show that quite surprisingly the addition of up to about 30 weight-% of a low-impact resin (Noan 80) to a high-impact butadiene-styrene resin (K-Resin®) having a bound butadiene content of about 32-34 weight-% and a bound styrene content of 66-88 weight-% improves the impact resistance of the latter at least 10%. Another, more general interpretation of the data of Table I shows that an improvement in Gardner impact of K-Resin® resin by the addition of styrene-methyl methacrylate copolymer (Noan 80) is attained at levels of about 22.5 to 34.0 weight percent of copolymerized butadiene based on the weight of the entire blend.

### EXAMPLE III

This example describes control blends comprising a commercial resinous, polymodal, radial butadiene-styrene copolymer, KR03 K-Resin® having a bound styrene content of 76 percent by weight, and a styrene-methyl methacrylate copolymer, Noan 80 having a bound styrene content of 80 percent by weight. The K-Resin® is commercially available from Phillips Petroleum Company and was prepared in accordance with the procedure described in Example I, except that the three incremental styrene additions were 68 lb., 38 lb., and 46 lb., respectively, and the amount of butadiene was 48 lb. Blending and molding conditions were essentially the same as those described in Example II.

Gardner impact data of the prepared blends listed in Table II, do not show the substantial improvement of at least 10 percent demonstrated by the blends of Example II. The slightly higher impact data of Runs 18 and 19 versus Run 17 are well within the experimental error of the test method.

TABLE II

Run	Weight-% of K-Resin® <sup>(1)</sup>	Weight-% of Noan 80 <sup>(2)</sup>	Weight-% of Butadiene in Blend <sup>(3)</sup>	Gardner Impact (cm · kg/mm) <sup>(4)</sup>
17 (Control)	100	0	24.0	59
18 (Control)	90	10	21.6	62
19 (Control)	80	20	19.2	63



TABLE II-continued

Run	Weight-% of K-Resin ® <sup>(1)</sup>	Weight-% of Noan 80 <sup>(2)</sup>	Weight-% of Butadiene in Blend <sup>(3)</sup>	Gardner Impact (cm · kg/mm) <sup>(4)</sup>
(Control)	70	30	16.8	45

<sup>(1)</sup> a resinous, polymodal, radial butadiene-styrene copolymer having a bound butadiene content of 24 weight percent, commercially produced and marketed by Phillips Petroleum Company, Bartlesville, OK.

<sup>(2)</sup> a styrene-methyl methacrylate copolymer having a bound styrene content of 80 weight percent.

<sup>(3)</sup>

$\frac{\text{weight-\% K-Resin } \textcircled{\text{R}} \text{ in blend}}{100} \times \text{weight-\% bound butadiene in K-Resin } \textcircled{\text{R}}$

<sup>(4)</sup> determined according to the modified ASTM D2444-70, procedure described in IG-1120 manual of Gardner Laboratories, using a 4 lb weight.

Reasonable variations and modifications are possible from the present invention without departing from the spirit thereof.

I claim:

1. A high impact resistant composition comprising a blend consisting of (a) a resinous, essentially non-elastomeric block copolymer of from 30-36 weight percent of a conjugated diene and from 64-70 weight percent of a vinylarene and (b) a copolymer consisting of a vinylarene and an acrylate, said blend having from about 21-34 total weight percent of said conjugated diene.

2. A high impact resistant composition according to claim 1 wherein said conjugated diene has from 4-12 carbon atoms per molecule and said vinylarene has from 8-20 carbon atoms per molecule.

3. A composition according to claim 1 wherein said resinous copolymer in (a) consists of from about 32-34 weight percent of said conjugated diene.

4. A composition according to claim 1 wherein (a) is a butadiene-styrene copolymer.

5. A composition according to claim 1 wherein (b) is a styrene-methyl methacrylate copolymer.

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[54] **BLENDS OF COPOLYMERS OF  
MONOVINYLARENES AND CONJUGATED  
DIENES CONTAINING TWO INTERIOR  
TAPERED BLOCKS**

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**C08L 53/02**

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**525/316**

[58] **Field of Search** ..... **525/98, 271, 314,**  
**525/316**

[56] **References Cited**

**U.S. PATENT DOCUMENTS**

4,704,434	11/1987	Kitchen	525/250
4,925,899	5/1990	Rendina	525/314
5,130,377	7/1992	Trepka	525/14
5,227,419	7/1993	Moczygemba	524/138
5,290,875	3/1994	Moczygemba	525/314
5,319,033	6/1994	Trepka	525/314
5,393,838	2/1995	Moczygemba	525/98

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[57] **ABSTRACT**

A method for preparing blends of a copolymer in a polymerization process by sequentially charging: (1) an initiator and monovinylaromatic monomer in the presence of a randomizer; (2) an initiator and monovinylaromatic monomer; (3) a mixture of monovinylaromatic and conjugated diene monomers; (4) a mixture of monovinylaromatic and conjugated diene monomers; (5) conjugated diene monomer; and (6) a coupling agent; and the polymodal tapered block copolymers prepared thereby. The copolymers are particularly useful neat or in blends for applications such as packaging and food or drink containers which require transparency and good environmental stress crack resistance.

**14 Claims, No Drawings**

# **BLENDS OF COPOLYMERS OF MONOVINYLARENES AND CONJUGATED DIENES CONTAINING TWO INTERIOR TAPERED BLOCKS**

This application is a Continuation application of Ser. No. 08/371,256 filed on Jan. 11, 1995, now abandoned, which is a divisional of application Ser. No. 08/162,735 filed on Dec. 2, 1993, now U.S. Pat. No. 5,399,628.

## **FIELD OF THE INVENTION**

This invention relates to tapered block copolymers of monovinylarenes and conjugated dienes and methods of preparation of these tapered block copolymers.

## **BACKGROUND OF THE INVENTION**

There has developed in the polymer field, and especially in the packaging and related industries, a need for thermoplastic polymers that can be formed into transparent articles having high impact strength with good environmental stress crack resistance. There are needs for polymers which are useful as single components as well as for use in blends to improve properties of articles made from other commonly used polymers. The polymers satisfying these needs should be suitable for use with conventional extrusion, injection and blow molding equipment and also suitable for use in other methods of forming plastics into containers, tubes, films, fibers, and the like. Polystyrene, high impact polystyrene, branched block copolymers, and the like have been developed to meet these criteria with various degrees of satisfaction.

Much effort has been directed to the preparation of substantially transparent block copolymer resins with a variety of block structures produced by a variety of monomer addition sequences and a variety of coupling agents.

Polymerization of styrene and butadiene with organolithium initiators to produce block copolymers in which one or more non-elastomeric polymer blocks are bonded to one or more elastomeric polymer blocks has been disclosed. Block copolymers have been formed by sequential charges of the monomers, sometimes followed by introduction of one or more coupling agents into the reaction. Tapered blocks in styrene/butadiene block copolymers have been prepared by simultaneous charging of monomers to the polymerization zone. Literally thousands of various combinations of sequences of charges of monomers and coupling agents are possible.

One problem encountered in making monovinylaromatic-conjugated diene block copolymers is control of the exothermic reaction temperatures and pressure which can rapidly reach high peaks if large monomer charges are made in order to produce large blocks in the copolymers.

## **SUMMARY OF THE INVENTION**

It is an object of this invention to provide improved resinous tapered block copolymers of vinyl-substituted aromatic hydrocarbons and conjugated dienes which can be used neat or in blends to make articles with improved environmental stress crack resistance and good impact strength.

A further object of this invention is to provide a process for making resinous tapered block copolymers of vinyl-substituted aromatic hydrocarbons and conjugated dienes. One purpose of this process is to avoid difficult-to-control

temperature and pressure extremes while producing monovinylaromatic/conjugated diene tapered blocks in copolymers with desirable properties.

In a preferred embodiment the inventive copolymers are prepared under solution polymerization conditions in a reaction zone by:

(a) charging a monovinylaromatic monomer and an initiator in the presence of a randomizer and allowing polymerization to occur until essentially no free monomer is present; thereafter

(b) charging an initiator and a monovinylaromatic monomer and allowing polymerization to occur until essentially no free monomer is present; thereafter

(c) charging a mixture of monovinylaromatic monomer and conjugated diene monomer and allowing polymerization to occur until essentially no free monomer is present; thereafter

(d) charging a mixture of monovinylaromatic monomer and conjugated diene monomer and allowing polymerization to occur until essentially no free monomer is present; thereafter

(e) charging a conjugated diene monomer and allowing essentially complete copolymerization to occur until essentially no free monomer is present; and thereafter

(f) charging the reaction mixture with a coupling agent.

## **DETAILED DESCRIPTION OF THE INVENTION**

We have discovered improved monovinylaromatic/conjugated diene tapered block copolymers which can be used neat or blended with polymers of styrene to produce resins which can be formed into articles with improved environmental stress crack resistance and good impact strength.

The polymers of this invention are characterized as resinous, non-rubbery polymodal block copolymers of at least one conjugated diene with at least one monovinylarene, having at least two random-tapered blocks and are prepared so that, when the choice of coupling agent permits, at least a portion of the final product is of a branched, coupled character.

The polymers prepared according to this invention contain from about 55 to about 95, preferably from about 60 to about 90, more preferably from about 65 to about 85, weight percent of copolymerized monovinyl substituted aromatic hydrocarbon monomer based on the weight of total monomers employed. Correspondingly, the inventive copolymers contain from about 45 to about 5, preferably from about 40 to about 10, and more preferably from about 35 to about 15 weight percent copolymerized conjugated diene monomer based on the total weight of monomers in the copolymer.

The coupled portions of the resinous polymodal block copolymers of this invention have terminal polymonovinylarene blocks on the extending arms of each linear or radial copolymer molecule, and further contain at least two central internal tapered blocks of monovinylarene and conjugated diene. The resinous copolymeric polymodal products also contain portions of linear uncoupled block copolymers of poly(monovinylarene)/poly(conjugated diene); the linear uncoupled block copolymer content is considered to be an important portion of the resinous product with respect to its overall properties.

## **Components**

The process of this invention can be carried out with any of the organomonoalkali metal compounds of the formula

RM wherein R is an alkyl, cycloalkyl or arylcarbanion containing 4 to 8 carbon atoms and M is an alkyl metal cation. The presently preferred initiators are alkylmonolithium compounds, especially n-butyllithium or sec-butyllithium.

The conjugated diene monomers which can be used contain 4 to 6 carbon atoms and include 1,3-butadiene, 2-methylene-1,3-butadiene, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene and 1,3-pentadiene and mixtures thereof. Each of the charges containing conjugated diene in the same sequence of charges may be the same, but are not necessarily the same, conjugated dienes or the same mixtures of conjugated dienes. Presently preferred conjugated diene monomer is 1,3-butadiene.

The monovinylaromatic monomers which can be used contain 8 to 12 carbon atoms and include styrene, alpha-methylstyrene, 4-methylstyrene, 3-methylstyrene, 2-methylstyrene, 4-ethylstyrene, 3-ethylstyrene, 2-ethylstyrene, 4-tert-butylstyrene, 2,4-dimethylstyrene and condensed aromatics such as vinyl naphthalene and mixtures thereof. Each of the charges containing monovinylaromatic monomer in the same sequence of charges may be the same but are not necessarily the same, monovinylaromatic monomer or mixture of monovinylaromatic monomers. The presently preferred monovinylaromatic monomer is styrene.

Examples of polar compounds which can be advantageously employed as randomizers and promoters of initiation in this invention are ethers, thioethers (sulfides) and tertiary amines. It is usually preferred to use ethers and sulfides in which the radicals attached to the oxygen or sulfur atoms are hydrocarbon radicals. Specific examples of such polar materials include dimethyl ether, diethyl ether, ethyl methyl ether, ethyl propyl ether, di-n-propyl ether, di-n-octyl ether, anisole, dioxane, 1,2-dimethoxyethane, dibenzyl ether, diphenyl ether, 1,2-dimethoxybenzene, tetramethylene oxide (tetrahydrofuran), potassium alkoxide, dimethyl sulfide, diethyl sulfide, di-n-propyl sulfide, di-n-butyl sulfide, methyl ethyl sulfide, dimethylethylamine, tri-n-propylamine, tri-n-butylamine, trimethylamine, triethylamine, tetramethylethylenediamine, tetraethylethylenediamine, pentamethyl-diethylenamine, N,N-di-methylaniline, N-methyl-N-ethylaniline, N-methyl-morpholine, and the like. Mixtures of these polar compounds also can be employed in the practice of the present invention. Presently preferred are either tetrahydrofuran or diethyl ether.

Among the suitable coupling agents are the di- or multivinylaromatic compounds, di- or multiepoxydes, di- or multiisocyanates, di- or multiimines, di- or multialdehydes, di- or multiketones, alkoxytin compounds, di- or multihalides, particularly silicon halides and halosilanes, mono-, di-, or multianhydrides, mono-, di-, or multiesters, preferably the esters of monoalcohols with polycarboxylic acids, diesters which are esters of monohydric alcohols with dicarboxylic acids, lactones, and the like, including compounds containing two or more groups and mixtures of two or more compounds.

Examples of suitable vinylaromatic coupling agents include, but are not limited to, divinylbenzene, 1,2,4-trivinylbenzene, 1,3-divinylnaphthalene, 1,3,5-trivinylnaphthalene, 2,4-divinylbiphenyl, p-diisopropenylbenzene, and the like. Of these, the divinylaromatic hydrocarbons are preferred, particularly divinylbenzene in either its ortho, meta, or para isomer. Commercial divinylbenzene which is a mixture of the three isomers and other compounds is satisfactory.

Epoxidized hydrocarbon polymers such as epoxidized liquid polybutadiene and epoxy compounds such as 1,2; 5,6; 9,10-triepoxydecane, and the like, can be used as coupling agents.

Organoalkyl phosphites, aryl phosphites and arylalkyl phosphites are considered useful as coupling agents in this invention.

Examples of suitable multiisocyanate coupling agents include benzene-1,2,4-trisocyanate, naphthalene-1,2,5,7-tetraisocyanate, and the like and mixtures thereof. Commercially available products known as PAPI-1, a polyarylpolyisocyanate having an average of 3 isocyanate groups per molecule and an average molecular weight of about 380 are suitable.

The multiimines, also known as multiaziridinyl compounds, such as those containing 3 or more aziridine rings per molecule, are useful as coupling agents. Other compounds useful as coupling agents include tetravinyl silane, trivinyl phosphine, the triaziridinyl phosphine oxides or sulfides such as tri(1-aziridinyl)phosphine oxide, tri(2-methyl-1-aziridinyl)-phosphine oxide, tri(2-ethyl-3-decyl-1-aziridinyl)phosphine sulfide, and the like and mixtures thereof.

The multialdehyde coupling agents are represented by compounds such as 1,4,7-naphthalenetetracarboxyaldehyde, 1,7,9-anthracenetetracarboxyaldehyde, 1,3,5-pentanetricarboxyaldehyde, and similar multialdehyde-containing aliphatic and aromatic compounds. The multiketones are represented by compounds such as 1,4,9,10-anthracenetetrone, 2,3-diacetoncyclohexanone, and the like. Examples of the multianhydrides include pyromellitic dianhydride, styrene-maleic anhydride copolymers, and the like. Examples of the multiesters include diethyladipate, triethylcitrate, 1,3,5-benzenetricarboxylic acid, triethyl ester, and the like. Mixtures of multialdehydes can be used.

Among the multihalide coupling agents are the silicon tetrahalides such as silicon tetrachloride, silicon tetrabromide, and silicon tetraiodide; the trihalosilanes such as trichlorosilane, trichloroethylsilane, tribromobenzylsilane, and the like; and the multihalogen-substituted hydrocarbons, such as 1,3,5-tri(bromomethyl)benzene, 2,5,6,9-tetrachloro-3,7-decadiene, and the like, in which the halogen is attached to a carbon atom which is alpha to an activating group such as an ether linkage, a carbonyl group, or a carbon-to-carbon double bond. Substituents inert with respect to lithium atoms in the terminally reactive polymer can also be present in the active halogen-containing compounds. Alternatively, other suitable reactive groups different from the halogens as described above can be present.

Other metal multihalides, particularly those of tin, lead, or germanium, can be employed as coupling and branching agents. Tri- and tetra-alkoxy tin compounds may be used. Silicon or other metal multialkoxides, such as silicon tetraethoxide, are also suitable coupling agents.

Examples of compounds containing more than one type of functional group include 1,3-dichloro-2-propanone, 2,2-dibromo-3-decanone, 2,4-dibromo-3-pentanone, 1,2; 4,5-diepoxy-3-pentanone, 1,2; 4,5-diepoxy-3-hexanone, 1,2; 11,12-diepoxy-8-pentadecanone, 1,3; 18,19-diepoxy-7,14-eicosanedione, and the like.

Useful multifunctional coupling agents include epoxidized vegetable oils such as epoxidized soybean oil, epoxidized linseed oil and the like or mixtures thereof.

The presently preferred coupling agent is epoxidized vegetable oil. Most preferred is epoxidized soybean oil.

The unique polymodal tapered block character of the polymer and improved environmental stress crack resistance of articles made from the polymer are produced by the unique sequences of an initial charge of monovinylaromatic monomer and initiator, preceding a second charge of initiator and monovinylaromatic monomer, followed by two separate charges of a mixture of monovinylaromatic monomer and conjugated diene, followed by a separate charge of conjugated diene monomer, and a subsequent coupling step.

The first initiator charge produces active living monovinyl aromatic component polymer blocks with alkali metal atoms (from the initiator) on at least one end to form active reaction sites. Each subsequent monomer charge adds monomer to the living polymer chain at the alkali metal reaction. At each stage of charging, polymerization is allowed to continue until essentially no free monomer is present.

With each subsequent charge which includes initiator a new polymer-lithium species will be produced, and each subsequent monomer charge has an opportunity for polymerization of part of the charge with each of the existing polymer-lithium species. Each of the active living polymer chains will be terminated on both ends with monovinyl aromatic blocks after polymerization of each monomer charge containing monovinyl aromatic. When mixtures of monovinyl aromatic monomer and conjugated diene are charged, the polymer chains will be terminated with the monovinyl aromatic rich ends of the tapered blocks prior to coupling. After virtually complete polymerization of the final monomer charge, the active living linear block copolymers are charged with at least one difunctional or polyfunctional coupling agent to allow coupling of each of the living species with each of the other living species or with others of the same living species to form the desired polymodal tapered block copolymers. If the coupling agent is not 100 percent efficient and/or if less or more than a stoichiometric amount is used, there can be some uncoupled terminated polymer chains of each of the species in the final reaction mixture.

Use of difunctional coupling agents will produce predominantly linear polymer chains. Depending upon functionality, various degrees and kinds of branching may be accomplished with polyfunctional coupling agents. Variations in the amount of a particular polyfunctional coupling agent also can be used to manipulate the degree and kind of branching at the coupling sites.

The charging sequence of this invention and the resulting polymers at each stage are exemplified using a selected monovinylaromatic monomer, conjugated diene and polyfunctional coupling agent in the following table.

TABLE 1

Invention Charging Sequence		
Step	Contents of Charge	Resulting Polymer Chains
(a)	randomizer, initiator <sub>1</sub> and styrene <sub>1</sub>	S <sub>1</sub> -Li <sub>1</sub>
(b)	initiator <sub>2</sub> and styrene <sub>2</sub>	S <sub>1</sub> -S <sub>2</sub> -Li <sub>1</sub> S <sub>2</sub> -Li <sub>2</sub>
(c)	butadiene <sub>1</sub> and styrene <sub>3</sub>	S <sub>1</sub> -S <sub>2</sub> -B <sub>1</sub> /S <sub>3</sub> -Li <sub>1</sub> S <sub>2</sub> -B <sub>1</sub> /S <sub>3</sub> -Li <sub>2</sub>
(d)	butadiene <sub>2</sub> and styrene <sub>4</sub>	S <sub>1</sub> -S <sub>2</sub> -B <sub>1</sub> /S <sub>3</sub> -B <sub>2</sub> /S <sub>4</sub> -Li <sub>1</sub> S <sub>2</sub> -B <sub>1</sub> /S <sub>3</sub> -B <sub>2</sub> /S <sub>4</sub> -Li <sub>2</sub>
(e)	butadiene <sub>3</sub>	S <sub>1</sub> -S <sub>2</sub> -B <sub>1</sub> /S <sub>3</sub> -B <sub>2</sub> /S <sub>4</sub> -B <sub>3</sub> -Li <sub>1</sub> S <sub>2</sub> -B <sub>1</sub> /S <sub>3</sub> -B <sub>2</sub> /S <sub>4</sub> -B <sub>3</sub> -Li <sub>2</sub>
(f)	epoxidized vegetable oil	polymodal tapered

TABLE 1-continued

Invention Charging Sequence	
	block polymers with styrene terminal blocks
where S = styrene	
B = butadiene	
B/S = tapered block	
Li = residue from a monoalkali metal initiator remaining on the end of the polymerization chain prior to termination or coupling.	
subscripts = designation of the numerical order in which that particular component was charged or formed.	

The randomizer is usually added with the diluent initially charged to the reactor. The third and fourth charges (c) and (d) which have two monomers may be either a mixture of the two monomers or simultaneous charging of two separate monomers.

As can be seen from the intermediate products listed in the charging sequence table above, there are at least two distinct species of polymer chains before coupling. Thus, polymodal tapered block copolymers comprising relatively high and low molecular weight species can be produced.

Tapered blocks in each of the growing polymer chains are produced by simultaneously charging with both monomers in the third and fourth steps shown in the preceeding table of a typical inventive charging sequence.

The randomizer regulates tapering or random polymerization of the monovinylaromatic monomer and the conjugated diene in a mixed monomer charge. Choice of randomizer can be used to manipulate the direction of taper in blocks resulting from charges of mixtures of monomers. The taper can be either a graduation from conjugated diene rich chain to monovinylaromatic rich chain or a graduation from a monovinylaromatic rich chain to conjugated diene rich chain according to which monomer enters the chain faster. For example, when tetrahydrofuran is used as a randomizer, the diene enters into the chain faster than the monovinyl substituted aromatic; therefore, when both the monovinylaromatic monomer and the conjugated diene are present, the block tapers gradually from an essentially polybutadiene block to an essentially monovinyl substituted aromatic polymer segment.

The weight ratio of monovinyl substituted aromatic monomer to conjugated diene monomer charged in steps (c) and (d) is from about 1:0.63 to about 1:2, preferably from about 1:0.67 to about 1:1.8, and more preferably from about 1:0.8 to about 1:1.5. The weight ratios of monovinyl substituted aromatic monomer to conjugated diene monomer in each of the two tapered blocks in the same polymer chain can be the same or different.

Generally each of the two tapered blocks made in steps (c) and (d) can be of about equal size; however, actual sizes of the two tapered blocks can vary within the same copolymer depending upon the amounts of monomers charged in each of the third and fourth monomer charges.

Prior to coupling, all of the living polymer chains have monovinylaromatic terminal blocks on one end because of the initial monovinylaromatic charge (a) and charge (b) made with initiator; the living ends of the chains prior to coupling will have conjugated diene blocks because of the fifth charge (e) containing only conjugated diene monomer.

In addition to the sequence of additions of the monomers and of the initiator, it is important to control the amount of each monomer and initiator addition at each stage or incre-

ment so that a suitable proportion of block sizes and proportion of polymodality is obtained. Generally in a presently preferred embodiment of this invention to obtain copolymers with a 75 weight percent polymerized monovinylaromatic content based on total weight of the copolymer, from about 27 to about 80 weight percent of the total weight percent of monovinylaromatic monomer is charged in step (a), from about 7 to about 33 weight percent of the total weight of monovinylaromatic monomer is charged in step (b), from about 5 to about 47 weight percent of the total weight of monovinylaromatic monomer is charged in step (c), and from about 5 to about 47 weight percent of the total weight percent of monovinylaromatic monomer is charged in step (d). Generally more preferably from about 40 to about 67 weight percent of the total weight percent of monovinylaromatic monomer is charged in step (a), from about 13 to about 27 weight percent of the total weight percent of monovinylaromatic monomer is charged in step (b), from about 8 to about 33 weight percent of the total weight percent of monovinylaromatic monomer is charged in step (c), and from about 8 to about 33 weight percent of the total weight percent of monovinylaromatic monomer is charged in step (d). Generally presently most preferably, from about 47 to about 60 weight percent of the total weight percent of monovinylaromatic monomer is charged in step (a), from about 16 to about 24 weight percent of the total weight percent of monovinylaromatic monomer is charged in step (b), from about 11 to about 29 weight percent of the total weight percent of monovinylaromatic monomer is charged in step (c), and from about 11 to about 29 weight percent of the total weight percent of monovinylaromatic monomer is charged in step (d).

It is feasible to stretch out over an interval of time the addition of one or more of the increments of initiator and/or the input of the appropriate monovinylarene monomer charge, thus spreading (increasing) further the polymodality of the resulting product upon coupling.

The polymerization process is carried out in a hydrocarbon diluent at any suitable temperature in a range of about  $-10^{\circ}$  to about  $150^{\circ}$  C., preferably in the range of about  $0^{\circ}$  to about  $110^{\circ}$  C., at pressures sufficient to maintain the reaction mixture substantially in the liquid phase. Temperatures and pressures will peak during polymerization of each monomer charge and then decrease when essentially no free monomer is left to react. Appropriate hydrocarbon diluents include linear and cycloparaffins such as butane, pentane, hexane, octane, cyclohexane, cyclopentane and mixtures thereof. Presently preferred is cyclohexane. Generally the choice of hydrocarbon or hydrocarbon mixture and temperature is such that the resulting polymer is in solution.

Small amounts of polar compounds are used to improve the effectiveness of alkylmonoalkali metal initiators such as *n*-butyllithium; dissociation of the alkylmonoalkali metal initiators affects the rate of initiation and polymerization. The polar compounds also affect partial randomization of the monovinylarene/conjugated diene so as to increase the random portion of the tapered block. The polar compounds are generally used in admixture with the hydrocarbon diluent.

The amounts of polar compounds used as randomizers and promoters of effectiveness of initiators in this invention will vary according to the reactivity and effectiveness of the particular randomizer used. For example, 1,2-dimethoxyethane, tetramethylethylenediamine and 1,2-dimethoxybenzene are much more efficient randomizers than most of the others listed above when used with the particular initiators and monomers used in the invention runs described below.

However, tetrahydrofuran is often used because the reaction will go nearer to completion in a shorter time after the initial reaction in the monomer rich environment. Also, there are dramatic variations in the amounts of each of these most efficient randomizers which will be needed. For example, for polymerizations such as those shown in the examples of invention runs in Table 4 of this application, much more tetrahydrofuran than 1,2-dimethoxyethane would be needed.

The amounts of polar compounds used as randomizers will also vary according to the desired molecular structure of the portions of tapered blocks which result from conjugated diene addition. For example, when using tetrahydrofuran, and 1,4 addition in excess of 1,2 addition is desired, then smaller amounts of the tetrahydrofuran would be used. In this example, when it is desirable that the tapered blocks of the polymer have more nearly equal amounts of 1,4 addition of butadiene and 1,2 addition of butadiene or only a little more 1,4 addition than 1,2 addition of butadiene, more of the tetrahydrofuran can be used.

When polymers with higher vinyl character resulting from 1,4 addition in excess of 1,2 addition are desired, then the useful amounts of tetrahydrofuran needed would be larger. However, use of too much randomizer can result in excessive polymer-lithium termination during polymerization and poor stability of the polymer or undesired side reactions, depending upon choice of randomizer. Use of too little randomizer would result in inefficient initiator use, broader molecular weight distribution and compositional variations.

The initial monovinylaromatic charge is made with the randomizer present for the additional effect of causing the monovinylaromatic component resulting from each initiator charge to be of relatively narrow molecular weight distribution. By varying the amounts of initiator in each of the two charges having initiator, the differences in molecular weights of the monovinylaromatic components resulting from each of the two charges can be increased.

Amounts of initiator employed are those which will produce resins with desirable melt flow which can be used neat or in blends to make articles with a good balance of properties including minimal blueness, good impact strength, good environmental stress crack resistance and flexural modulus. Presently preferred are amounts of initiator in each of the two initiator charges sufficient to obtain a block copolymer having a melt flow ranging from about 2 to about 50 g/10 minutes, more preferably from about 3 to about 40 g/10 minutes, and most preferably from about 4 to about 30 g/10 minutes, as determined by ASTM D1238-73, condition 200° C./5.0 kg. The amounts of initiator contemplated as useful in each of the two charges having initiator are shown in Table 2.

Use of too small an amount of initiator would result in high molecular weight polymers. Conversely, use of too large an amount of initiator would result in polymers having short chain polymeric species and low molecular weight.

The weight ratio of the amounts of initiator in each of the charges having initiator can be represented as 1:0.25-300.

$$Li_1:Li_2::1:0.25-300$$

wherein  $Li_1$ =initiator in the first charge

$Li_2$ =initiator in the second charge

More preferably for most applications, the amount of initiator in the second charge of initiator is from about 0.75 to about 10.0 times, based on weight, as much as the amount of initiator in the first initiator charge. Presently most preferred is an amount of initiator in the second charge which is from about 0.9 to about 5 times, based on weight, as much as the amount of initiator in the first initiator charge.

Varying the weight ratios of the initiator charges will result in variations of the proportionate amounts of species present in the copolymer. Other factors affecting the proportionate amounts of species present in the copolymer include presence of impurities and/or scavengers in the reactor, effectiveness of the polar randomizer as a promoter, choice of coupling agent(s), and polymerization temperature.

The polymerization is carried out in a substantial absence of oxygen and water, preferably under an inert gas atmosphere. Prior to the coupling step, the reaction mass contains a very high percentage of molecules (polymer chains) in which an alkali metal cation is positioned at one end of each polymer chain. Impurities in the feed such as water or alcohol reduce the amounts of monoalkali metal polymer in the reaction mass.

After essentially complete polymerization of the final charge added to the polymer reaction, one or more suitable difunctional or polyfunctional coupling agents is added. As used here, the term "coupling" means the bringing together and joining, by means of one or more central coupling atoms or coupling moieties, two or more of the living monoalkali metal-terminated polymer chains. A wide variety of compounds for such purposes can be employed.

Any effective amount of the coupling agent can be employed. While the amount is not believed to be particularly critical, a stoichiometric amount relative to the active polymer-alkali metal tends to promote maximum coupling as a generality. Presently preferred is an amount of coupling agent slightly greater than stoichiometric relative to the active polymer-alkali metal. However, less than stoichiometric amounts can be used for higher degrees of coupling where desired for particular products of broadened molecular weight distribution.

Typically, the total amount of coupling agent is in the range of about 0.005 to 10 phm (parts per 100 parts of total monomer employed in the polymerization). Presently preferred when most combinations of monomers and coupling agents are used is about 0.2 to about 0.6 phm of coupling agent, depending upon amounts of initiator used. Presently most preferred is about 0.3 to about 0.5 phm, depending upon amounts of initiator used. Use of an amount of a reasonably high efficiency coupling agent within these ranges provides polymers with a moderately broad molecular weight distribution. Use of an insufficient amount of coupling agent will result in less complete coupling of the living polymer chains and, depending upon choice of coupling agent, more branching; use of an excessive amount of coupling agent will have the same result.

At the conclusion of the coupling process, the coupled polymer may still contain bound polymeric alkali metal alkoxides depending on the type of coupling agent employed. The system is treated with an active compound such as water, alcohol, phenols, carbon dioxide or linear saturated aliphatic mono- and dicarboxylic acids to remove any remaining alkali metal from the copolymer chain.

While the polymer product is still in solution, stabilization agents can be added. Additional stabilizers could be added during finishing before pelletizing. This treatment will provide oxidative stability for the polymer during processing and handling and subsequent long term use.

Commonly used stabilization processes can use a combination of compounds, including, but not limited to, a hindered phenol and an organophosphite, particular examples of which are octadecyl 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate and tris-nonylphenylphosphite.

After stabilization, the hydrocarbon diluent is then flashed from the polymer solution to increase the solids content. The

polymer cement, i.e. the polymer in the polymerization solvent, usually contains about 10 to 40, more usually 20 to 35, weight percent solids, the balance solvent. Preferably, but not necessarily, the polymer cement is flashed to remove by evaporation a portion of the solvent so as to reduce the solvent content to a concentration of about 0 to 50, more usually about 0 to 10, weight percent (corresponding to a solids content of about 100 to 50, more usually about 100 to 90, weight percent).

Flashing of the polymer cement may be followed by desolventizing extrusion with vacuum in commercial production or by other vacuuming processes to achieve consistent solvent content of less than 0.3 weight percent.

The resinous copolymeric products can be, and normally are, compounded with anti-oxidants, anti-blocking agents, release agents and other additives, as known in the compounding arts.

A typical charging sequence and useful ranges of amounts of the charges is given in Table 2.

TABLE 2

Ranges of Amounts of Components  
in a Typical Invention Charging Sequence\*

Step	Component <sup>b</sup>	Broad Range <sup>c</sup>	Preferred Range <sup>c</sup>	More Preferred Range <sup>c</sup>
(a)	randomizer <sup>d</sup>	0.001-3	0.005-1.5	0.015-0.3
	initiator and monovinylarene monomer	0.005-1.5 20-60	0.01-1.0 30-50	0.02-0.1 35-45
(b)	initiator and monovinylarene monomer	0.005-1.5 5-25	0.01-1.0 10-20	0.02-0.1 12-18
(c)	monovinylarene monomer and conjugated diene monomer	4-35 4-35	6-25 6-25	8-22 8-22
(d)	monovinylarene monomer and conjugated diene monomer	4-35 4-35	6-25 6-25	8-22 8-22
(e)	conjugated diene monomer	1-10	2-8	4-6
(f)	coupling agent	0.005-10	0.2-0.6	0.3-0.5

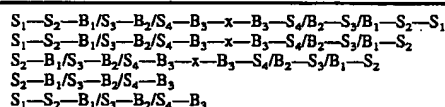
\*Charges of monomer and initiator are made in the presence of an amount of diluent or solvent sufficient to prevent excessive heat of reaction.

<sup>b</sup>Monomers within each charge having more than one monomer can be added simultaneously or as a mixture, slowly or quickly. Randomizer in charge (a) may be already present in the diluent or added as a separate charge.

<sup>c</sup>Ranges of amounts are given in parts by weight per 100 parts by weight of total monomers (phm).

<sup>d</sup>To achieve high vinyl content, up to 3 phm randomizer may be used.

After coupling, at least the following coupled and uncoupled polymeric species are present in the polymer of the invention:



wherein

S=monovinylaromatic block

B=conjugated diene block

B/S=tapered block

x=residual coupling agent or coupling site

subscripts=indications of the charges which are the source of the polymer blocks.

Depending upon choice and amount of coupling agent or agents and whether coupling agents are charged as a mixture or incrementally, there can be present other polymeric species with varying degrees of branching.

#### Blends

The resinous polymodal copolymer products of this invention can be blended with other styrenic polymers such as polystyrene acrylonitrile-butadiene-styrene copolymers (ABS), styrene-acrylonitrile copolymers (SAN) and other styrene copolymers. When less transparency is desired or if transparency is not necessary, the invention copolymers can be blended with polyolefins and/or olefin copolymers.

Blends of the invention copolymers with polymers of styrene are particularly useful applications for the improved tapered block copolymers of this invention. Articles made from these blends have surprisingly good environmental stress crack resistance and other advantageous properties such as transparency and impact strength. For example, articles made from blends of styrene homopolymer and polymers of this invention typically are transparent and have good impact strength and have dramatically improved environmental stress crack resistance.

The presently preferred polymers of styrene employed in the blends of this invention are usually (a) homopolymers of styrene; or (b) copolymers of styrene as a major component with a minor amount of any other copolymerizable monovinylaromatic compound other than styrene, such as alpha-methylstyrene, vinyltoluene or para-tert-butyl styrene. A minor amount of other monomers such as methyl acrylate, methyl methacrylate, acrylonitrile and the like can be copolymerized with the styrene.

The invention copolymers can be blended with styrene resins made in bulk polymerization. These resins are commonly prepared by heating styrene and any comonomer at temperatures in the range of 100° to 200° C. with application of pressure, if necessary, to combine the monomers. The polymerization can also be carried out at lower temperatures by the addition of free-radical generating peroxidic catalysts such as benzoyl peroxide, acetyl peroxide, di-t-butyl peroxide and the like. Alternatively, the polymerization can be carried out in suspension to yield a dry powder or in emulsion, usually resulting in a latex of polystyrene which can be coagulated to yield the solid powdery polystyrene. The polymerization can also be carried out in solution with precipitation of the product, if desired. Solvent can be removed by standard techniques such as steamstripping or solvent evaporation.

High impact polystyrene (HIPS) can be successfully employed in blends with the invention copolymers. Suitable high impact polystyrenes can be prepared by polymerizing styrene in the presence of an elastomer, typically polybutadiene rubber. In these resins the styrene forms a continuous phase throughout which the rubber particles are dispersed.

The blends of this invention can be prepared by any suitable means including blending, tumbling and extrusion. Examples of these methods include, but are not limited to, dry mixing in the form of a powder or pellets, wet mixing in the form of a solution or slurry, and melt extrusion compounding.

The polymers and any other ingredients or additives may be mechanically blended together in the desired proportions with the aid of any suitable mixing device conveniently used for mixing rubbers or plastics, such as, for example, a differential roll mill, a Banbury mixer, or an extruder.

In these types of methods the polymers and any other components and additives used can be in any form, such as, for example, fluff, powder, granulate, pellet, solution, slurry, and/or emulsion. Any additive can be combined with the polymers according to any method known in the art. Examples of incorporation methods include, but are not limited to, dry mixing in the form of a powder and wet mixing in the form of a solution or slurry.

Melt extrusion compounding can be carried out using any suitable method such as in single screw or twin screw extruders or other melt extruders at temperatures above the melting point or glass transition temperature of the polymers.

The presently preferred method comprises blending the polymers in powder or granulate form and extruding the blend in sheet form to feed a thermoforming or direct feed to an injection or blow molder.

In order to facilitate thorough mixing of the polymers and to develop the desired combination of physical properties, pellets are generally metered by loss-in-weight feeders or by screw feeders at a temperature low enough to avoid softening the pellets. The metered pellets are dropped into an extruder which melts and blends the components to provide a homogeneous melt.

Alternatively, solution blending methods known in the art may be used.

The ranges of amounts of polymers useful in blends varies according to the properties and economics desired. For example, when an invention copolymer is blended with a polymer of styrene, practical ranges include using amounts such as from about 5 to about 95 weight percent polymer of styrene, more usually from about 15 to about 90 weight percent polymer of styrene, and most preferably from about 30 to about 80 weight percent polymer of styrene with the balance being one or more of the polymodal resinous copolymer products of this invention. For a more particular example, when an invention copolymer is blended with general purpose polystyrene, broad ranges include using amounts such as from about 10 to about 90 weight percent polystyrene, more usually from about 20 to about 85 weight percent polystyrene, and most preferably from about 40 to about 70 weight percent polystyrene with the balance being one or more of the polymodal resinous copolymer products of this invention. Generally, use of too much of the invention copolymers in a blend would result in good properties but loss of economic advantage. Use of too little of the invention copolymers in a blend would result in loss of impact resistance. These blends can be economical ways of gaining the desirable attributes of both polystyrene and the invention polymers while maintaining good environmental stress crack resistance in articles made from the blends.

The compositions of this invention or blends thereof can be extruded, thermoformed, injection molded, blow molded, or made into films or sheets. Articles made from the compositions of this invention are transparent, have excellent environmental stress crack resistance to fats and oils, and have other physical properties within acceptable ranges for such applications as drinking cups, lids, bottles, other food containers, medical drainage units, shrink wrap and over wrap. Articles made from blends of this invention can economically provide advantageous properties for similar applications.

#### Test Procedures

The environmental stress crack resistance potential of the block copolymers was determined in an accelerated test



referred to as the Puncture Test. Test specimens about 2 inches (50 mm) square were cut from an interior layer about 0.015 inches (0.4 mm) thick from a coil or roll of extruded sheet. The side of the film or sheet facing away or furthest from the center of the coil or roll, of course, must "stretch" or cover more distances than the side closest to the center of the coil or roll. Results obtained from the outside part of a rolled layer are termed "curl down" and those from the inside part are termed "curl up".

Each specimen was clamped over a hole about 25 mm in diameter and 4 drops of soybean oil was placed on the specimen over the hole. A rounded tipped stainless steel rod about 1/2 cm in diameter was weighted with a 2 kg load and brought into contact with the specimen. The time to failure in minutes was recorded. Ten specimens of each run were tested and the results were averaged.

The puncture test results appear to correlate well with other environmental stress crack resistance test results and are obtained more quickly.

Except as noted in the examples, melt flows were measured using an extrusion Plastometer from Tinius Olson Testing Machine Co., at 200° C. with a 4.9 kg weight.

Other properties of test specimens were tested using ASTM procedures shown in Table 3.

TABLE 3

Test Procedures Used	
Property	ASTM Method
Flow rate, g/10 min	D 1238-88
Condition 200° C./5.0 kg	
Haze, %	D 1003-61 (1990)
Transmittance, %	D 1003-61 (1990)
Shore D hardness	D 2240-91
Tensile strength at yield and break, MPa	D 638-91 at 50 mm/min Type I test specimens
Elongation at yield and break, %	D 638-91 at 50 mm/min
Flexural modulus, MPa	D 790-86
Izod impact strength, notched, J/m	D 256-88
Vicat softening point, °C.	D 1525-91
Total energy dart drop, J	D 4272-85

## EXAMPLES

The following examples will describe in more detail the experimental process used and the resinous polymodal tapered block copolymers with vinylarene terminal blocks obtained as a result of the process, and blends made with the invention copolymers. These examples should be taken as illustrative and not restrictive.

Styrene and butadiene were chosen as monomers to exemplify the invention, and randomizer, initiator, coupling agent and diluent appropriate for these monomers were used. Quantities of reagents are usually expressed in parts per hundred monomer (phm) based on the total weight of monovinylarene and conjugated diene employed.

## Example I

This example describes four invention polymerization runs (runs, 1, 2, 3, 4) that were carried out to produce resinous polymodal coupled tapered block styrene/butadiene copolymers with resinous terminal blocks. Styrene (from Stirling Chemical) and 1,3-butadiene (from Texas El Paso) were dried by passage over activated alumina (Kaiser A-201), and then copolymerized and coupled in a 6-stage

process using n-butyllithium initiator (from Lithium Corporation in America).

Polymerization runs were carried out under nitrogen in a stirred, jacketed, stainless steel 7.6-liter reactor employing essentially anhydrous reactants and conditions. The anhydrous mixtures were stirred continuously during the polymerization process. The cyclohexane diluent, which contained 0.04 phm tetrahydrofuran (THF) in each polymerization except in Example IV, was preheated to about 50° C. before monomers were charged to the reactor. The n-butyllithium was charged as a 2 weight percent solution in cyclohexane. In polymerization steps in which both butadiene and styrene were charged, they were charged simultaneously as a mixture.

In the coupling step, the Vikoflex® 7170 coupling agent used was an epoxidized vegetable oil commercially available from Viking Chemical Company. In the terminating step, carbon dioxide from a pressurized container was admitted to provide about 0.4 phm carbon dioxide to the reactor. Water was also added in an amount slightly in stoichiometric excess of the initiator to separate the lithium residues from the polymer chains.

The antioxidant mixture added in the stabilizing step contained a hindered phenol [octadecyl 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate, commercially available as Irganox® 1076 from Ciba-Geigy] and an organic phosphite (tris-nonylphenyl phosphite, available as TNPP from GE Specialty Chemicals). Each stabilizer was dissolved separately in cyclohexane and mixed together. Enough of the mixture was added to the reactor to provide 0.25 phm hindered phenol and 1 phm organic phosphite. In Runs 1 and 2 a microcrystalline wax (BE Square® 195) was also added as an antiblocking agent.

After each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 10–20 phm cyclohexane solvent and cleared with a nitrogen sparge.

Following the stabilization step, each copolymer solution was flashed at 178° C.–180° C. to remove a portion of the diluent. Substantially all of the remaining diluent was removed in a vacuum oven by drying at 90° C. for one hour. The resulting polymer was chopped in a granulator into crumb size and then dried for an additional hour in a vacuum oven.

In each of the four runs (1, 2, 3, and 4), 2000 g total monomers (butadiene and styrene) were used. About 76 weight percent of the total amount of cyclohexane diluent (3130 g) was charged initially. The remaining cyclohexane diluent was added during the run as a diluent or flush for the various reactants added in subsequent steps. In these four polymerizations, the weight ratio of monomers charged was 75/25 styrene/butadiene.

The charges and the results of the runs are summarized in Table 4. Tapered butadiene/styrene segments were formed in steps 3 and 4 by charging both butadiene and styrene monomers.

The charging sequence used was i, S<sub>1</sub>, i, S<sub>2</sub>, B<sub>1</sub>/S<sub>3</sub>, B<sub>2</sub>/S<sub>4</sub>, B<sub>3</sub>, coupling agent. The monomer weight ratios corresponding to the S<sub>1</sub>, S<sub>2</sub>, B<sub>1</sub>/S<sub>3</sub>, B<sub>2</sub>/S<sub>4</sub>, B<sub>3</sub> sequence were 40, 15, 10/10, 10/10, 5. Weight ratios of amounts of initiator used in the first two polymerization steps of each of the four runs was kept constant at 1:2.33.

The devolatilized copolymers from runs 1, 2, 3 and 4 were designated invention copolymers 1, 2, 3 and 4, and had melt flows of 8.4, 7.5, 7.2 and 7.1 g/10 min, respectively.

Invention resin A was prepared by dry blending samples of the copolymers from runs 1, 2, 3 and 4 in equal amounts. Resin A had a melt flow of 7.7 g/10 min.

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TABLE 4

Invention Runs - Polymer A				
Components <sup>a</sup>	Run 1	Run 2	Run 3	Run 4
<u>Step 1</u>				
Cyclohexane, phm	152	152	152	152
Tetrahydrofuran, phm	0.04	0.04	0.04	0.04
n-Butyllithium initiator, phm	0.03	0.03	0.03	0.030
Styrene, phm	40	40	40	40
Polymerization Time, min	12	12	12	12
Peak Polymerization Temperature, °C.	94.6	88.7	90.8	88.3
Peak Polymerization Pressure, psi	30	30	30	30
<u>Step 2</u>				
n-Butyllithium initiator, phm	0.07	0.07	0.07	0.07
Styrene, phm	15	15	15	15
Polymerization Time, min	12	12	14	12
Peak Polymerization Temperature, °C.	84.4	77.8	78.1	78.3
Peak Polymerization Pressure, psi	40	30	40	40
<u>Step 3</u>				
Butadiene, phm	10	10	10	10
Styrene, phm	10	10	10	10
Polymerization Time, min	20	20	20	20
Peak Polymerization Temperature, °C.	96.7	84.8	86.7	84.8
Peak Polymerization Pressure, psi	50	40	40	40
<u>Step 4</u>				
Butadiene, phm	10	10	10	10
Styrene, phm	10	10	10	10
Polymerization Time, min	20	20	20	20
Peak Polymerization Temperature, °C.	103.7	104.1	104.6	104.8
Peak Polymerization Pressure, psi	60	55	60	60
<u>Step 5</u>				
Butadiene, phm	5	5	5	5
Polymerization Time, min	12	19	10	10
Peak Polymerization Temperature, °C.	92.9	89.5	96	91.4
Peak Polymerization Pressure, psi	100	100	100	100
<u>Step 6 (Coupling)</u>				
Vikoflex 7170, phm	0.3	0.3	0.3	0.3
Time, min	16	16	16	16
Temperature, °C.	93.5	99	95	86
Pressure, psi	100	80	100	100
<u>Step 7 (Terminating)</u>				
Water, phm	0.2	0.2	0.2	0.2
Carbon Dioxide, phm	0.4	0.4	0.4	0.4
Time, min	25	25	25	25
Temperature, °C.	97	95	98	99
Pressure, psi	90	70	75	90
<u>Step 8 (Stabilizing)</u>				
Stabilizer Mixture, phm	1.25	1.25	1.25	1.25
Be Square 195, phm	0.0015	0.0015	0.0015	0.0015
Time, min	5	5	5	5
Temperature, °C.	94	101	95	100
Pressure, psi	1.25	125	125	125
<u>Recovered Resin</u>				
Melt Flow, g/10 min	8.4	7.5	7.2	7.1

<sup>a</sup>After each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 3-20 phm cyclohexane diluent and cleared with nitrogen.

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Example II

Two comparison copolymers were prepared to demonstrate the importance of the structural features of the invention copolymers for environmental stress crack resistance. In these two comparison polymers styrene to butadiene weight ratio of the charged monomers was 74.4 to 25.5.

Copolymers 5, 6, 7 and 8 were made with one initial styrene charge, two tapered butadiene/styrene blocks, and no terminal butadiene segment prior to coupling. The polymerization charges and results are summarized in Table 5. These four copolymers were dry blended to form comparison resin B, which had a melt flow of 7.2 g/10 min.

Copolymers 9, 10, 11 and 12 were prepared with styrene, styrene, butadiene, styrene, and butadiene segments, in that sequence, and then coupled. These copolymers contain no tapered blocks. The polymerization charges and results are shown in Table 6. These four copolymers were dry blended to yield comparison resin C, which had a melt flow of 7.7 g/10 min.

TABLE 5

Comparison Runs - Polymer B				
Components <sup>a</sup>	Run 5	Run 6	Run 7	Run 8
<u>Step 1</u>				
Cyclohexane, phm	205	205	205	205
Tetrahydrofuran, phm	0.04	0.04	0.04	0.04
n-Butyllithium initiator, phm	0.03	0.03	0.03	0.030
Styrene, phm	40.1	40.1	40.1	40.1
Polymerization Time, min	12	12	12	12
Peak Polymerization Temperature, °C.	83	85	82	76
<u>Step 2</u>				
Butyllithium initiator, phm	0.03	0.03	0.03	0.03
Butadiene, phm	8	8	8	8
Styrene, phm	19.7	19.7	19.7	19.7
Polymerization Time, min	40	40	40	40
Peak Polymerization Temperature, °C.	86	86	87	79
<u>Step 3</u>				
n-Butyllithium initiator, phm	0.05	0.05	0.05	0.05
Butadiene, phm	17.5	17.5	17.5	17.5
Styrene, phm	14.6	14.6	14.6	14.6
Polymerization Time, min	40	40	40	40
Peak Polymerization Temperature, °C.	106	106	109	100
<u>Step 4 (Coupling)</u>				
Vikoflex 7170, phm	0.4	0.4	0.4	0.4
Time, min	16	16	16	16
Temperature, °C.	90	88	90	95
<u>Step 5 (Terminating)</u>				
Water, phm	0.2	0.2	0.2	0.2
Carbon Dioxide, phm	0.4	0.4	0.4	0.4
Time, min	25	25	25	25
Temperature, °C.	88	82	85	85
<u>Step 6 (Stabilizing)</u>				
Stabilizer Mixture, phm	1.25	1.25	1.25	1.25
Time, min	5	5	5	5
Temperature, °C.	87	83	85	88
<u>Recovered Resin</u>				
Melt Flow, g/10 min	7.3	6.8	7.1	7.5

<sup>a</sup>After each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 3-20 phm cyclohexane diluent and cleared with nitrogen.

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TABLE 6

Comparison Runs - Polymer C				
Components <sup>a</sup>	Run 9	Run 10	Run 11	Run 12
<u>Step 1</u>				
Cyclohexane, phm	145	145	145	145
Tetrahydrofuran, phm	0.04	0.04	0.04	0.04
n-Butyllithium initiator, phm	0.03	0.03	0.03	0.030
Styrene, phm	40.1	40.1	40.1	40.1
Polymerization Time, min	12	12	12	12
Peak Polymerization Temperature, °C.	79	80	81	85
<u>Step 2</u>				
n-Butyllithium initiator, phm	0.03	0.03	0.03	0.03
Styrene, phm	19.7	19.7	19.7	19.7
Polymerization Time, min	12	12	14	12
Peak Polymerization Temperature, °C.	77	76	76	76
<u>Step 3</u>				
Butadiene, phm	8	8	8	8
Polymerization Time, min	16	16	16	16
Peak Polymerization Temperature, °C.	79	72	72	72
<u>Step 4</u>				
n-Butyllithium, phm	0.105	0.105	0.105	0.105
Styrene, phm	14.6	14.6	14.6	14.6
Polymerization Time, min	12	12	12	12
Peak Polymerization Temperature, °C.	79	94	92	81
<u>Step 5</u>				
Butadiene, phm	17.5	17.5	17.5	17.5
Polymerization Time, min	16	16	16	16
Peak Polymerization Temperature, °C.	94	95	95	94
<u>Step 6 (Coupling)</u>				
Vikoflex 7170, phm	0.39	0.39	0.39	0.39
Time, min	16	16	16	16
Temperature, °C.	84	81	80	86
<u>Step 7 (Terminating)</u>				
Water, phm	0.2	0.2	0.2	0.2
Carbon Dioxide, phm	0.4	0.4	0.4	0.4
Time, min	25	25	25	25
Temperature, °C.	81	81	85	86
<u>Step 8 (Stabilizing)</u>				
Stabilizer Mixture, phm	1.25	1.25	1.25	1.25
Time, min	5	5	5	5
Temperature, °C.	88	82	83	82
Pressure, psi	125	125	125	125
<u>Recovered Resin</u>				
Melt Flow, g/10 min	6.4	7.2	7.7	6.7

<sup>a</sup>After each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 3–20 phm cyclohexane diluent and cleared with nitrogen.

## Example III

Another comparative copolymer 13 without tapered styrene butadiene blocks was used for comparison with the invention resins. The comparative polymodal, coupled block copolymer of styrene and butadiene was essentially the same as the invention copolymer except that sequential butadiene and styrene charges were used in place of the mixture of butadiene and styrene used in the invention copolymer. This comparative copolymer was prepared from about 75 weight percent styrene and about 25 weight percent butadiene and was polymodal before coupling. Similar charges of initiator and randomizer were used. The monomer addition

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sequences were S, S, B, S, B in weight ratios of 40, 20, 7.5, 15, 17.5, respectively, followed by coupling. Comparative copolymer 13 had a melt flow of 7.0 g/10 min and was designated Resin D.

## Example IV

Three comparative copolymers (14, 15 and 16) were prepared to demonstrate the importance of using two rather than one charges of mixtures of monomers next preceding the coupling step in the invention copolymer. Both polymerizations were carried out with a total monomer charge of 1500 g. About 79 weight percent of the cyclohexane diluent (3720 g) was charge initially. The rest of the diluent was added during the run as a diluent or flush for the other reactants. n-Butyllithium was used as the initiator in these polymerizations and THF was used as the randomizer.

Copolymers 14, 15, and 16 were prepared with one initial styrene charge, one styrene/butadiene tapered block, and a final butadiene segment next preceding the coupling step. Table 7 describes the charges and results of these polymerizations. The styrene to butadiene weight ratio of the charged monomers was 75 to 25.

Comparative Resin E was prepared by dry blending samples of the copolymers from runs 14, 15 and 16 in equal amounts. Resin E had a melt flow of 7.2 g/10 min.

TABLE 7

Comparative Runs - Resin E				
Components <sup>a</sup>	Run 14	Run 15	Run 16	
<u>Step 1</u>				
Cyclohexane, phm	152	152	152	
Tetrahydrofuran, phm	0.04	0.04	0.04	
n-Butyllithium initiator, phm	0.03	0.03	0.03	
Styrene, phm	40	40	40	
Polymerization Time, min	10	10	10	
Peak Polymerization Temperature, °C.	86.7	82.4	83.6	
Peak Polymerization Pressure, psi	30	40	30	
<u>Step 2</u>				
n-Butyllithium initiator, phm	0.07	0.07	0.07	
Styrene, phm	15	15	15	
Polymerization Time, min	10	10	10	
Peak Polymerization Temperature, °C.	78.1	78.1	76.9	
Peak Polymerization Pressure, psi	40	40	40	
<u>Step 3</u>				
Butadiene, phm	20	20	20	
Styrene, phm	20	20	20	
Polymerization Time, min	20	20	20	
Peak Polymerization Temperature, °C.	120.3	115.0	113.3	
Peak Polymerization Pressure, psi	60	70	80	
<u>Step 4</u>				
Butadiene, phm	5	5	5	
Polymerization Time, min	19	10	10	
Peak Polymerization Temperature, °C.	92.8	88	85.9	
Peak Polymerization Pressure, psi	100	90	100	
<u>Step 5 (Coupling)</u>				
Vikoflex 7170, phm	0.4	0.4	0.4	
Time, min	16	16	16	
Temperature, °C.	92.5	92	96	
Pressure, psi	70	90	100	
<u>Step 6 (Terminating)</u>				
Water, phm	0.2	0.2	0.2	
Carbon Dioxide, phm	0.4	0.4	0.4	

TABLE 7-continued

Comparative Runs - Resin E			
Components <sup>a</sup>	Run 14	Run 15	Run 16
Time, min	25	25	25
Temperature, °C.	94.1	96	92
Pressure, psi	70	50	50
Step 7 (Stabilizing)			
Stabilizer Mixture, phm	1.25	1.25	1.25
Time, min	5	5	5
Temperature, °C.	95	97.2	93
Pressure, psi	125	125	125
Recovered Resin			
Melt Flow, g/10 min	9.8	7.0	6.5

<sup>a</sup>After each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 3-20 phm cyclohexane diluent and cleared with nitrogen.

## Example V

Each of Resins A (from runs 1, 2, 3, 4), B (from runs 5, 6, 7, 8), C (from runs 9, 10, 11, 12), D (a commercial resin), and E (from runs 14, 15, 16) were analyzed for styrene and butadiene content.

One-gram samples of each of the resins tested were dissolved in 10 ml of toluene and precipitated with about 25 ml of isopropanol. The solids from each sample were isolated, then redissolved in about 10 ml of deuterated chloroform. The chloroform solutions were dried overnight in a vacuum oven at 40° C. Half of each of the dried samples was then redissolved in more deuterated chloroform and oven dried at 40° C. for 4 to 5 hours. The redried samples were then redissolved in an amount of deuterated chloroform sufficient to form 15 weight percent solutions which were run in 5 mm NMR tubes at ambient temperature in a Varian EM-390 instrument with <sup>1</sup>H frequency of 90 MHz in the continuous wave mode. Concentrations of styrene and butadiene were calculated by integrating the areas under peaks representing proton concentrations of components in the samples.

Results of the NMR analysis are reported in weight percents in Table 8.

TABLE 8

Resin Analysis <sup>a</sup>					
	Inven- tion Resin A	Com- pari- son Resin B	Com- pari- son Resin C	Com- pari- son Resin D	Com- pari- son Resin E
Melt flow, g/10 min	7.7	7.2	7.7	7.0	7.2
Mw/Mn, thousands	—	184/124	160/160	—	—
Heterogeneity Index	—	1.84	1.51	—	—
Total styrene, wt %	75.9	76.2	76.1	—	74.9
Blocked styrene, wt %	66.3	64.0	71.9	—	65.2
1,2-Butadiene, wt %	3.5	4.7	3.3	—	3.7
1,4-Butadiene, wt %	19.9	19.1	20.5	—	20.5

<sup>a</sup>Wt % determined by NMR analysis.

## Example VI

This example compares results of puncture tests of films made from invention Resin A from Example I with results of puncture tests of films made from comparative Resins B and C from Example II, and D and E from Examples III and IV. Each sample was converted into sheet form by melt extrusion at a temperature of about 175°-185° C. using a sheet die and a cooled polishing roll. Puncture testing was done as described above. Longer test times indicate that the sample has more environmental stress crack resistance than samples with shorter test times.

The comparative test results are presented in Table 9. These results show that invention Resin A had an enhanced resistance to environmental stress cracking relative to comparative resins without tapered styrene/butadiene segments (Resin C and D), comparative Resin E with only one tapered block and a final butadiene block next preceding coupling and comparative Resin B which has two tapered blocks, but only one initiator charge and no butadiene block next preceding coupling.

TABLE 9

Puncture Test Results of Neat Resins						
Resin	Source	Type	MF, g/10 min	Thick- ness, mils	Puncture Test, min <sup>a</sup>	
					Curl Up	Curl Down
A	Ex. I	Invention	7.1	15	178	190
B	Ex. II	Comparative	7.2	15	3.0	5.0
C	Ex. II	Comparative	7.7	16	6.0	8.2
D	Ex. III	Comparative	7.0	16	4.4	4.6
E	Ex. IV	Comparative	7.2	20	11	14.7

<sup>a</sup>Test method described in the specifications. Higher numbers indicate more environmental stress crack resistance.

## Example VII

In this example samples of the invention resin from Example I comparison resins from Examples II, III and IV were each blended with general purpose polystyrene so that blend properties could be compared. Each of the blends contained 40 wt % general purpose polystyrene (Novacor® 555 commercially available from Novacor) and 60 wt % of the monovinylaromatic-conjugated diene copolymer.

Polymer pellets were dry blended then melt extruded in a Werner-Pfleiderer ZSK-30 vented twin-screw extruder with screw feeder (equipment?) using an open vent and a barrel temperature of 210° C. The extruded polymer blend was converted into sheet form by melt extrusion at a temperature of about 175°-185° C. using a sheet die and a cooled polishing roll.

Puncture testing of each of the sample sheets was done as described in the puncture test procedure detailed above. Longer test times indicate that the sample has more environmental stress crack resistance than samples with shorter test times. The comparative test results are presented in Table 10. These results show that blends made with invention Resin A had an enhanced resistance to environmental stress cracking relative to blends made with the comparative Resin D which had no tapered styrene/butadiene blocks, and E with a single large tapered styrene/butadiene block.

The other samples were not tested as blends because their initial neat puncture test values were so low and values always drop significantly when blended with polystyrene.

TABLE 10

Puncture Tests Results of Blends <sup>a</sup>				
60:40 Invention Resin:GPPS		Thick- ness,  mils	Puncture Test, min <sup>b</sup>	
Blend	Type		Curl Up	Curl Down
A	Invention	14	11	9.9
D	Comparative	16.5	1.2	1.4
E	Comparative	17	1.2	1.4

<sup>a</sup>No blends were made of Resin B and Resin C.

<sup>b</sup>Test method described in the specifications. Higher numbers indicate more environmental stress crack resistance.

While the polymers and methods of this invention have been described in detail for the purpose of illustration, the inventive polymers and methods are not to be construed as limited thereby. This patent is intended to cover all changes and modifications within the spirit and scope thereof.

That which is claimed is:

1. Blends of at least one polymer of styrene and a copolymer prepared by a method of preparing copolymers under polymerization conditions in a reaction zone comprising:

(a) charging a monovinylaromatic monomer and an initiator and in the presence of a randomizer, allowing polymerization to occur until essentially no free monomer is present; thereafter

(b) charging an initiator and a monovinylaromatic monomer and allowing polymerization to occur until essentially no free monomer is present; thereafter

(c) charging a mixture of monovinylaromatic monomer and conjugated diene monomer and allowing polymerization to occur until essentially no free monomer is present; thereafter

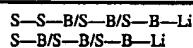
(d) charging a mixture of monovinylaromatic monomer and conjugated diene monomer and allowing polymerization to occur until essentially no free monomer is present; thereafter

(e) charging a conjugated diene monomer and allowing essentially complete polymerization to occur until essentially no free monomer is present; and thereafter

(f) charging reaction mixture with a coupling agent, wherein only two initiator charges are present and are performed as stated in steps (a) and (b).

2. Articles made from the blend of claim 1.

3. Blends of at least one polymer of styrene and a polymodal coupled resinous block copolymer of a monovinylaromatic compound and a conjugated diene, said copolymer having polymer chains which result from coupling



wherein S=monovinylaromatic block

B=conjugated diene block

B/S=tapered block of B and S

Li=living polymer site or coupling site.

4. Articles made from the blend of claim 3.

5. A blend as recited in claim 1 wherein said polymer of styrene is one chosen from (a) homopolymers of styrene; or (b) copolymers of styrene as a major component with a minor amount of any other copolymerizable monovinylaromatic compound other than styrene.

6. A blend as recited in claim 3 wherein said polymer of styrene is one chosen from (a) homopolymers of styrene; or (b) copolymers of styrene as a major component with a minor amount of any other copolymerizable monovinylaromatic compound other than styrene.

7. A blend as recited in claim 5 wherein said polymer of styrene is a homopolymer of styrene.

8. A blend as recited in claim 6 wherein said polymer of styrene is a homopolymer of styrene.

9. A blend as recited in claim 5 wherein said polymer of styrene is one chosen from polyalpha-methylstyrene, polypara-tert-butylstyrene and polyvinyltoluene.

10. A blend as recited in claim 6 wherein said polymer of styrene is one chosen from polyalpha-methylstyrene, polypara-tert-butylstyrene and polyvinyltoluene.

11. Blends of a polymer chosen from the group of high impact polystyrene, acrylonitrile-butadiene-styrene copolymers, styrene-acrylonitrile copolymers, styrene-methylacrylate copolymers and styrene-methyl-methacrylate copolymers and a copolymer prepared by a method of preparing copolymers under polymerization conditions in a reaction zone comprising:

(a) charging a monovinylaromatic monomer and an initiator and in the presence of a randomizer, allowing polymerization to occur until essentially no free monomer is present; thereafter

(b) charging an initiator and a monovinylaromatic monomer and allowing polymerization to occur until essentially no free monomer is present; thereafter

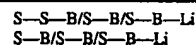
(c) charging a mixture of monovinylaromatic monomer and conjugated diene monomer and allowing polymerization to occur until essentially no free monomer is present; thereafter

(d) charging a mixture of monovinylaromatic monomer and conjugated diene monomer and allowing polymerization to occur until essentially no free monomer is present; thereafter

(e) charging a conjugated diene monomer and allowing essentially complete polymerization to occur until essentially no free monomer is present; and thereafter

(f) charging reaction mixture with a coupling agent, wherein only two initiator charges are present and are performed as stated in steps (a) and (b).

12. Blends of a polymer chosen from the group of high impact polystyrene, acrylonitrile-butadiene-styrene copolymers, styrene-acrylonitrile copolymers, styrene-methylacrylate copolymers and styrene-methyl-methacrylate copolymers and a polymodal coupled resinous block copolymer of a monovinylaromatic compound and a conjugated diene, said copolymer having polymer chains which result from coupling



wherein S=monovinylaromatic block

B=conjugated diene block

B/S=tapered block of B and S

Li=living polymer site or coupling site.

13. Articles made from the blend of claim 11.

14. Articles made from the blend of claim 12.

\* \* \* \* \*



US006107411A

**United States Patent** [19]

Toya et al.

[11] **Patent Number:** **6,107,411**[45] **Date of Patent:** **Aug. 22, 2000**

[54] **BLOCK COPOLYMER, BLOCK COPOLYMER COMPOSITION AND HEAT SHRINKABLE FILMS MADE THEREOF**

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[52] **U.S. Cl.** ..... **525/316; 525/88; 525/89; 525/97; 525/98; 525/99**

[58] **Field of Search** ..... **525/316, 88, 89, 525/97, 98, 99**

[56] **References Cited****U.S. PATENT DOCUMENTS**

4,386,125	5/1983	Shiraki et al.	
5,189,110	2/1993	Ikematu et al.	
5,319,033	6/1994	Trepka et al.	525/314
5,554,697	9/1996	Van Dijk et al.	525/316
5,583,182	12/1996	Asahara et al.	525/314

**FOREIGN PATENT DOCUMENTS**

0 740 214	10/1996	European Pat. Off.
WO 95/33006	12/1995	WIPO

**OTHER PUBLICATIONS**

Patent Abstracts of Japan, vol. 95, No. 7, Aug. 31, 1995, JP 07 097419, Apr. 11, 1995.

Patent Abstracts of Japan, vol. 95, No. 11, Dec. 26, 1995, JP 07 216186, Aug. 15, 1995.

Patent Abstracts of Japan, vol. 97, No. 1, Jan. 31, 1997, JP 08 225712, Sep. 3, 1996.

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[57] **ABSTRACT**

A block copolymer (hereinafter referred to as the block copolymer (I)), consisting essentially of a vinyl aromatic hydrocarbon and a conjugated diene and satisfying the following conditions (1) to (5):

- (1) the weight ratio of vinyl aromatic hydrocarbon units to conjugated diene units is from 60:40 to 90:10,
- (2) the number average molecular weight of the block copolymer is from 40,000 to 500,000,
- (3) the ratio of E'30/E'10, where E'30 is the storage modulus at a temperature of 30° C. and E'10 is the storage modulus at a temperature of 10° C., is from 0.75 to 1,
- (4) the block proportion of a vinyl aromatic hydrocarbon polymer contained in the block copolymer is from 70 to 100%, provided the block proportion=W1/W0×100, where W1 is the weight of block polymer chains of the vinyl aromatic hydrocarbon in the block copolymer, and W0 is the total weight of the vinyl aromatic hydrocarbon units in the block copolymer, and
- (5) chains consisting of from 1 to 3 repeating units of the vinyl aromatic hydrocarbon contained in the block copolymer, are not more than 25%, based on the above W0.

**7 Claims, No Drawings**

# BLOCK COPOLYMER, BLOCK COPOLYMER COMPOSITION AND HEAT SHRINKABLE FILMS MADE THEREOF

The present invention relates to a block copolymer consisting essentially of a vinyl aromatic hydrocarbon and a conjugated diene, which is excellent in transparency, stiffness, impact resistance and spontaneous shrinkage resistance, a composition comprising such a block copolymer, and heat shrinkable films prepared by orienting them.

It is known that when a vinyl aromatic hydrocarbon and a conjugated diene are subjected to block copolymerization by living anion polymerization in an organic solvent using an alkyl lithium as an initiator, the structure of the copolymer can be diversified by a method of e.g. changing the weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene or changing the manner of addition, whereby block copolymers having various physical properties can be obtained. In general, a block copolymer is a polymer having excellent impact resistance and transparency. If the content of the conjugated diene in the block copolymer is large, the copolymer tends to be a thermoplastic elastomer. On the other hand, if the content of the vinyl aromatic hydrocarbon is large, the copolymer tends to show characteristics as thermoplastics. To utilize such excellent characteristics of the block copolymer, various production methods have been disclosed, for example, in JP-B-36-19286 and JP-B-48-4106. Further, the block copolymer has not only such excellent characteristics but also excellent compatibility with various vinyl aromatic hydrocarbon polymers and thus is useful for reinforcement, which is disclosed, for example, in JP-B-45-19388, JP-B-47-43618 and JP-B-51-27701.

However, such block copolymers and their compositions have had a drawback that they are inferior in spontaneous shrinkage resistance, although they are relatively transparent and have good impact resistance. Accordingly, when they are oriented to be used as heat shrinkable films, the films tend to undergo substantial shrinkage (spontaneous shrinkage) while they are left to stand still. Therefore, they have had problems that they can not be fixed as labels on various bottles or printings thereon tend to be dislocated. Therefore, it has been desired to develop a heat shrinkable film having the spontaneous shrinkage resistance improved, and a block copolymer or a block copolymer composition suitable for such a heat shrinkable film.

Under these circumstances, the present inventors have conducted an extensive study to obtain a heat shrinkable film having improved spontaneous shrinkage resistance and as a result, have found that a block copolymer having a specific weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene in the block copolymer, a specific molecular weight of the block copolymer, a specific storage modulus, a specific block proportion of the vinyl aromatic hydrocarbon polymer and a specific proportion of chains consisting of repeating units of the vinyl aromatic hydrocarbon, or a block copolymer composition having a certain specific vinyl aromatic hydrocarbon polymer mixed thereto, satisfies the object, and that by using such a block copolymer or a block copolymer composition, it is possible to obtain the desired heat shrinkable film having improved spontaneous shrinkage resistance. The present invention has been accomplished on the basis of these discoveries.

That is, the present invention provides a block copolymer (hereinafter referred to as the block copolymer (I)) consisting essentially of a vinyl aromatic hydrocarbon and a

conjugated diene and satisfying the following conditions (1) to (5) or such a block copolymer satisfying the following condition (6) in addition to the conditions (1) to (5), and a heat shrinkable film made of such a block copolymer.

(1) The weight ratio of vinyl aromatic hydrocarbon units to conjugated diene units is from 60:40 to 90:10.

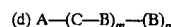
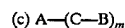
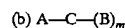
(2) The number average molecular weight of the block copolymer is from 40,000 to 500,000.

(3) The ratio of E30/E10, where E30 is the storage modulus at a temperature of 30° C. and E10 is the storage modulus at a temperature of 10° C., is from 0.75 to 1.

(4) The block proportion of a vinyl aromatic hydrocarbon polymer contained in the block copolymer is from 70 to 100%, provided the block proportion =  $W1/W0 \times 100$ , where W1 is the weight of block polymer chains of the vinyl aromatic hydrocarbon in the block copolymer, and W0 is the total weight of the vinyl aromatic hydrocarbon units in the block copolymer.

(5) Chains consisting of from 1 to 3 repeating units of the vinyl aromatic hydrocarbon contained in the block copolymer, are not more than 25%, based on the above W0.

(6) The structure of the block copolymer (I) is represented by one of the following formulae:



where A is a polymer chain of the vinyl aromatic hydrocarbon, B is a copolymer chain of the vinyl aromatic hydrocarbon and the conjugated diene, C is a polymer chain of the conjugated diene, m is an integer of at least 2, and n is an integer of at least 1.

Further, the present invention provides a block copolymer composition comprising the block copolymer (I) and the following polymer (II), and a heat shrinkable film made thereof:

(II) at least one polymer selected from the group consisting of (i) a block copolymer consisting essentially of a vinyl aromatic hydrocarbon and a conjugated diene, which is different from the block copolymer (I) as defined in claim 1 or 2, (ii) a vinyl aromatic hydrocarbon polymer, (iii) a copolymer consisting essentially of a vinyl aromatic hydrocarbon and a (meth)acrylate, and (iv) a rubber-modified styrene type polymer.

The block copolymer composition preferably comprises from 50 to 99.8 parts by weight of the block copolymer (I) and from 0.2 to 50 parts by weight of the polymer (II), provided that the total amount of the polymers (I) and (II) is 100 parts by weight, and when the polymer (II) is the rubber-modified styrene type polymer (iv), the amount of the polymer (iv) is not more than 20 parts by weight.

Now, the present invention will be described in detail with reference to the preferred embodiments.

The vinyl aromatic hydrocarbon to be used for the production of the block copolymer (I) of the present invention may, for example, be styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, α-methylstyrene, vinyl naphthalene or vinyl anthracene. Particularly, styrene is commonly used.

The conjugated diene to be used for the production of the block copolymer (I) of the present invention may, for example, be 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene or

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1,3-hexadiene. Particularly, 1,3-butadiene or isoprene is commonly used.

The weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene is from 60:40 to 90:10, preferably from 70:30 to 85:15. If the vinyl aromatic hydrocarbon is less than 60%, the transparency and stiffness of the block copolymer tend to be low, and if it exceeds 90%, the impact resistance tends to be low, whereby the copolymer tends to be not practically useful.

The number average molecular weight of the block copolymer (I) is usually from 40,000 to 500,000, preferably from 80,000 to 300,000. If it is less than 40,000, no adequate stiffness or impact resistance of the block copolymer tends to be obtained, and if it exceeds 500,000, the processability tends to be low, such being undesirable.

In the present invention, the number average molecular weight of the block copolymer was determined by a conventional method using gel permeation chromatograph (hereinafter referred to simply as GPC).

The ratio of E'30/E'10, where E'30 is the storage modulus of the block copolymer at 30° C. and E'10 is the storage modulus of the block copolymer at a temperature of 10° C., which is the most remarkable characteristic of the block copolymer (I) of the present invention, is from 0.75 to 1, preferably from 0.8 to 1. If it is less than 0.75, the spontaneous shrinkage tends to be large, and the copolymer may not be practically useful as a heat shrinkable film. The block copolymer of the present invention undergoes no crosslinking reaction or the like at a temperature of 30° C., and the ratio of E'30/E'10 will accordingly be not higher than 1. The storage modulus is a value measured by a dynamic viscoelasticity measuring apparatus.

The block proportion of the vinyl aromatic hydrocarbon of the block copolymer (I) is usually from 70 to 100 wt %, preferably from 75 to 100 wt %. If the block proportion is less than 70 wt %, the transparency and stiffness tend to be low, such being undesirable.

The block proportion of the vinyl aromatic hydrocarbon is one obtained by the following formula.

$$\text{Block proportion (\%)} = W1/W0 \times 100$$

where W1 is the weight of block polymer chains of the vinyl aromatic hydrocarbon in the block copolymer, and W0 is the total weight of the vinyl aromatic hydrocarbon units in the block copolymer.

W1 in the above formula, was obtained by subjecting the block copolymer to ozonolysis by a method disclosed in a literature (Y. Tanaka, et al., "RUBBER CHEMISTRY AND TECHNOLOGY", 58, p.16 (1985)), measuring the obtained vinyl aromatic hydrocarbon polymer components by GPC, obtaining molecular weights corresponding to the respective peaks of the chromatogram from a calibration curve prepared by using standard polystyrene and styrene oligomer, and quantitatively analyzing those exceeding a number average molecular weight of 3,000 from the respective peak areas. As the detector for GPC measurement, an ultraviolet spectrophotometer having the wavelength set at 254 nm, was used.

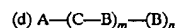
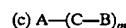
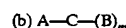
The proportion of chains consisting of from 1 to 3 repeating units (hereinafter referred to as s1 to s3) of the vinyl aromatic hydrocarbon in the block copolymer (I), is desired to be not more than 25%, based on the total weight of the vinyl aromatic hydrocarbon units in the block copolymer. If the proportion of s1 to s3 chains exceeds 25%, spontaneous shrinkage tends to be substantial, such being undesirable. The proportion of s1 to s3 chains is obtained by the following formula.

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Proportion (%) of S1 to s3 chains =  $W2/W0 \times 100$  where W2 is the weight of s1 to s3 in the block copolymer, and W0 is the total weight of the vinyl aromatic hydrocarbon units in the block copolymer.

W2 in the above formula was obtained by measuring the ozonolysis products obtained by the above mentioned method, by means of a column with an exclusion limit of 3,000 by GPC, identifying the obtained peaks by the method disclosed in a literature (Y. Tanaka, "Encyclopedia of Engineering Materials, (Part A)", 1, p.677 (1988)), and quantitatively measuring their peak areas.

The structure of the block copolymer (I) is preferably one represented by one of the following formulae:



where A is a polymer chain of the vinyl aromatic hydrocarbon, B is a copolymer chain of the vinyl aromatic hydrocarbon and the conjugated diene, C is a polymer chain of the conjugated diene, m is an integer of at least 2, and n is an integer of at least 1.

In the above formulae, A is a polymer chain of the vinyl aromatic hydrocarbon and thus represents a block polymer chain of the vinyl aromatic hydrocarbon, which can be introduced by polymerizing one or more types of the above mentioned vinyl aromatic hydrocarbons.

In the above formulae, B is a copolymer chain of the vinyl aromatic hydrocarbon and the conjugated diene. The plurality of B in the above formulae may be the same or different from one another in their molecular weights or the compositional distributions (the distributions of the vinyl aromatic hydrocarbon and the conjugated diene). The distributions may be random or graded i.e. the distribution densities of the vinyl aromatic hydrocarbon units and the conjugated diene units may be graded.

B can be introduced by copolymerizing the above vinyl aromatic hydrocarbon and the conjugated diene. At that time, the molecular weights and the compositional distributions can be controlled under definite polymerization conditions mainly by adjusting the amounts of the monomers and the manner of their addition.

In the above formulae, C is a polymer chain of the conjugated diene and thus represents a block polymer chain of the conjugated diene. It can be introduced by polymerizing one or more types of the above mentioned conjugated dienes. When a plurality of C are present in the formulae, the respective molecular weights may be the same or different.

Now, the method for producing the block copolymer (I) of the present invention will be described.

The block copolymer (I) can be produced by polymerizing monomers of the vinyl aromatic hydrocarbon and the conjugated diene in an organic solvent using a organic lithium compound as an initiator. The organic solvent may, for example, be an aliphatic hydrocarbon such as butane, pentane, hexane, isopentane, heptane, octane or isooctane, an alicyclic hydrocarbon such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane or ethylcyclohexane, or an aromatic hydrocarbon such as benzene, toluene, ethylbenzene or xylene.

The organic lithium compound is a compound having at least one lithium atom bonded in its molecule. For example, it is a monofunctional organic lithium compound such as



n-propyl lithium, isopropyl lithium, n-butyl lithium, sec-butyl lithium or tert-butyl lithium, or a polyfunctional organic lithium compound such as hexamethylene dilithium, butadienyl dilithium or isoprenyl dilithium.

As the aromatic hydrocarbon and the conjugated diene to be used in the present invention, those mentioned above, can be used. For each of the vinyl aromatic hydrocarbon and the conjugated diene, one or more types may be selected for use for polymerization. In so-called living anionic polymerization using the above organic lithium compound as an initiator, the vinyl aromatic hydrocarbon and the conjugated diene subjected to the polymerization reaction will be converted to a polymer substantially in their entire amounts.

In the present invention, the molecular weight of the block copolymer (I) can be controlled by adjusting the amount of the initiator added to the total amount of the monomers.

In the present invention, the ratio (E'30/E'10) of the storage modulus at a temperature of 30° C. (E'30) to the storage modulus at a temperature of 10° C. (E'10) can be adjusted by controlling the weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene in the block copolymer (I), the molecular weights or the compositional distributions of A, B and C in the above mentioned formulae, the block proportion of the copolymer, and the s1 to s3 chain proportions.

The block proportion and the s1 to s3 chain proportion in the block copolymer (I) can be controlled by adjusting the amount of a randomization agent used at the time of copolymerizing the vinyl aromatic hydrocarbon with the conjugated diene. As such a randomization agent, tetrahydrofuran (THF) is mainly used, but an ether, an amine, a thioether, a phosphoramidate, an alkylbenzene sulfonate, or a potassium or sodium alkoxide may, for example, be also used. Useful ethers include, in addition to the above mentioned THF, dimethyl ether, diethyl ether, diphenyl ether, diethylene glycol dimethyl ether, and diethylene glycol diethyl ether, diethylene glycol dibutyl ether. The amine may, for example, be a tertiary amine such as trimethylamine, triethylamine or tetramethylethylenediamine, or a cyclic amine. Further, triphenylphosphine, hexamethylphosphoramide, a potassium or sodium alkylbenzene sulfonate, or a potassium or sodium butoxide, may also be used as a randomization agent.

The amount of the randomization agent is preferably from 0.001 to 10 parts by weight per 100 parts by weight of the total charged monomers. The timing of the addition may be prior to the initiation of the polymerization reaction or prior to the polymerization of the copolymer chain —B—. Further, it may be additionally added, as the case requires.

Further, the block proportion and the s1 to s3 chain proportion can be controlled also by continuously feeding the vinyl aromatic hydrocarbon and the conjugated diene mechanically to the polymerization reactor, or alternately adding the vinyl aromatic hydrocarbon and the conjugated diene to the polymerization reactor in divided small portions.

The block copolymer (I) thus obtained is inactivated by adding a polymerization terminating agent such as water, an alcohol or carbon dioxide in an amount sufficient to inactivate the active terminals. A method for recovering the copolymer from the obtained block copolymer solution may, for example, be (A) a method of precipitating it by a poor solvent such as methanol, (B) a method of precipitating it by evaporating the solvent by e.g. a heat roll (a drum drier method), (C) a method of removing the solvent by a vented extruder after concentrating the solution by a concentrator, or (D) a method of dispersing the solution in water, and

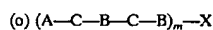
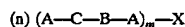
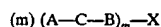
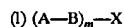
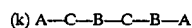
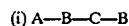
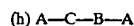
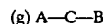
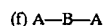
blowing steam thereinto to heat and remove the solvent and to recover the copolymer (a steam stripping method).

Now, the polymer (II) to be used in the present invention, will be described.

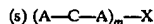
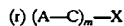
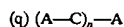
The polymer (II) to be used in the present invention is at least one polymer selected from the group consisting of (i) a block copolymer consisting essentially of a vinyl aromatic hydrocarbon and a conjugated diene, which is different from the block copolymer (I), (ii) a vinyl aromatic hydrocarbon polymer, (iii) a copolymer consisting essentially of a vinyl aromatic hydrocarbon and a (meth)acrylate, and (iv) a rubber-modified styrene type polymer.

As the block copolymer (i), one prepared by polymerizing the vinyl aromatic hydrocarbon and the conjugated diene in a weight ratio of 60:40 to 90:10, is used. The number average molecular weight is not particularly limited, but is preferably from 40,000 to 500,000. Such a block copolymer can be prepared by polymerization in an organic solvent using an organic lithium compound as an initiator, in the same manner as for the above mentioned block copolymer (I), and the organic solvent, the initiator, the vinyl aromatic hydrocarbon, the conjugated diene and the randomization agent to be used, may be those which are described above.

The structure of this block copolymer (i) may take any form so long as the above requirements are satisfied. Preferred examples include structures having copolymer segments as shown by the following formulae:



and those having the following complete block structures:



In the above formulae, A, B, C, m and n are as defined above, and when a plurality of A are present in the formulae, they are molecular weights may be the same or different from one another. Further, X represents a residue of the above mentioned polyfunctional organic lithium compound to be used as an initiator, or a residue of a polyfunctional coupling agent. The polyfunctional coupling agent may, for example, be silicon tetrachloride or epoxylized soybean oil.

As the vinyl aromatic hydrocarbon polymer (ii), a homopolymer of a vinyl aromatic hydrocarbon as described

for the production of the block copolymer (I), or a copolymer of two or more such vinyl aromatic hydrocarbons may be employed. Particularly, polystyrene may be mentioned as a common one.

The copolymer (iii) consisting essentially of a vinyl aromatic hydrocarbon and a (meth)acrylate is one which maintains transparency even when mixed with the block copolymer (I). It may be obtained by polymerizing the vinyl aromatic hydrocarbon as described for the production of the block copolymer (I), with a (meth)acrylate. The (meth)acrylate may, for example, be methyl acrylate, ethyl acrylate, butyl acrylate, isobutyl acrylate, hexyl acrylate, (2-ethyl)hexyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate or (2-hydroxy)ethyl methacrylate.

Such a copolymer (iii) can be obtained by polymerizing a monomer mixture comprising a vinyl aromatic hydrocarbon and a (meth)acrylate in a weight ratio of from 5:95 to 99:1, preferably from 40:60 to 99:1, more preferably from 70:30 to 99:1.

The rubber-modified styrene type polymer (iv) can be obtained by polymerizing a vinyl aromatic hydrocarbon or a monomer copolymerizable therewith, in the presence of various elastomers. As the vinyl aromatic hydrocarbon, those described above for the production of the block copolymer (I), may be employed. As the monomer copolymerizable therewith, (meth)acrylic acid or a (meth)acrylate may, for example, be employed. As the elastomer, butadiene rubber, styrene-butadiene rubber, styrene-butadiene block copolymer elastomer, chloroprene rubber or natural rubber may, for example, be employed. A particularly preferred rubber-modified styrene type polymer may be high impact polystyrene (HIPS).

The block copolymer composition of the present invention comprises the block copolymer (I) and the polymer (II). It is preferably a block copolymer composition comprising from 50 to 99.8 parts by weight of the block copolymer (I) and from 0.2 to 50 parts by weight of the polymer (II), provided that the total amount of the polymers (I) and (II) is 100 parts by weight. The polymer (i) is used for improvement of stiffness and impact resistance, and it is used preferably in an amount of from 0.2 to 50 parts by weight, more preferably from 0.2 to 40 parts by weight, in the total amount. If it is less than 0.2 part by weight, no adequate effect of its addition tends to be observed, and if it exceeds 50 parts by weight, spontaneous shrinkage of a heat shrinkable film obtainable from such a block copolymer composition tends to be substantial, such being undesirable. The polymer (ii) or (iii) is used for improvement of stiffness, and it is preferably used in an amount of from 0.2 to 50 parts by weight, more preferably from 0.2 to 30 parts by weight, in the total amount. If it is less than 0.2 part by weight, no adequate effect of its addition tends to be observed, and if it exceeds 50 parts by weight, stiffness tends to be high, whereby there will be a problem that orientation tends to be difficult. The polymer (iv) is used for improvement of stiffness and impact resistance, and it is preferably used in an amount of from 0.2 to 20 parts by weight, more preferably from 0.2 to 10 parts by weight, in the total amount. If it is less than 0.2 part by weight, no adequate effect of its addition tends to be observed, and if it exceeds 20 parts by weight, transparency tends to deteriorate to a practically useless level. When it is used for improvement of the slipping property of the film, it may be incorporated in an amount of from 0.2 to 5 parts by weight.

In order to effectively use the block copolymer composition of the present invention in various fields, various

additives may be incorporated as the case requires. The additives include, for example, various stabilizers, lubricants, processing aids, antiblocking agents, antistatic agents, antifog agents, light stabilizers softening agents, plasticizers, and pigments. Such additives may be added to the block copolymer solution or may be blended with a recovered copolymer, followed by melt mixing.

The stabilizers include, for example, phenol type antioxidants such as 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, and 2,6-di-tert-butyl-4-methylphenol, and phosphorus-type antioxidants such as trisnonylphenyl phosphite. As the antiblocking agent, the antistatic agent or the lubricant, a fatty acid amide, ethylenebisstearamide, sorbitane monostearate, a saturated fatty acid ester of an aliphatic alcohol, or a pentaerythritol fatty acid ester, may, for example, be mentioned. Such additives are used preferably within a range of at most 5 wt % relative to the block copolymer.

The composition of the present invention can be obtained by mixing the block copolymer (I) and the polymer (II). The mixing method may be any conventional method. For example, it may be dry-blended by e.g. a Henschel mixer, a ribbon blender, a supermixer or a V-blender. Further, it may be melted and pelletized by an extruder. Melt mixing is particularly preferred. Further, it is possible to employ a method in which the polymer solutions are mixed to each other, whereupon the solvent is removed.

The heat shrinkable film of the present invention can be obtained by uniaxially, biaxially or multi-axially orienting a sheet or film obtained by extruding the above described block copolymer composition by a conventional method such as a T-die technique or a tubular technique. As an example of uniaxial orientation, a method of orienting an extruded sheet by a center in a direction perpendicular to the direction for extrusion, or a method of orienting an extruded tubular film in a circumferential direction, may be mentioned. As an example of biaxial orientation, a method of orienting an extruded sheet by a roll in the direction for extrusion and then by e.g. a center in a direction perpendicular to the direction for extrusion, or a method of orienting an extruded tubular film in the direction for extrusion and in the circumferential direction simultaneously or sequentially, may be mentioned.

In the present invention, the temperature for orientation is preferably from 60 to 120° C. If it is lower than 60° C., the sheet or film is likely to break during orientation, and if it exceeds 120° C., a good shrinkable property tends to be hardly obtainable. The orientation ratio is not particularly limited, but is preferably from 1.5 to 8 times. If it is less than 1.5 times, the heat shrinkability tends to be inadequate, and if it exceeds 8 times, orientation tends to be difficult. When such a film is to be used as a heat shrinkable label or wrapping material, the heat shrinkability is required to be at least 20% at 80° C. If the heat shrinkability is less than 20%, a high temperature will be required for shrinkage, whereby an article to be wrapped is likely to be adversely affected. The thickness of the film is preferably from 10 to 300  $\mu$ m.

The heat shrinkable film of the present invention is useful particularly for a heat shrinkable label or a heat shrinkable cap seal, but it is also suitable for use as a wrapping film or the like.

Now, the present invention will be described in detail with reference to Examples. However, it should be understood that the present invention is by no means restricted by the following Examples.

The structural characteristics and physical properties shown in Tables 1 to 7, were Measured by the following methods.

(1) Number average molecular weight: Measured by a GPC method under the following conditions:

(A) Measuring apparatus: "SHODEX SYSTEM-21", manufactured by Showa Denko K. K.

(B) Column: "PL gel MIXED-B", manufactured by POLYMER LABORATORY INC., three columns

(C) Solvent: Tetrahydrofuran

(D) Quantitative determination: A calibration curve was prepared by using standard polystyrene.

(2) Storage modulus: Measured by using a viscoelasticity spectrometer "DMS210", manufactured by Seiko Denshi K. K., at a frequency of 1 Hz at temperatures of 30° C. and 10° C.

(3) Haze: Measured in accordance with ASTM D1003 (thickness of the test specimen: 2 mm). The lower the haze, the better the transparency.

(4) Tensile modulus: Measured in accordance with JIS K6871. A test specimen of No. 1 type was used, and a test speed of F was employed. The higher the tensile modulus, the higher the stiffness.

(5) Izod impact strength: Measured in accordance with JIS K6871. A test specimen of No. 2A was used. The higher the Izod impact strength, the higher the impact resistance.

(6) Heat shrinkability: An oriented film was immersed in a warm water of 80° C. for 30 seconds, whereupon the heat shrinkability was calculated by the following formula:

$$\text{Heat shrinkability (\%)} = (L1 - L2) / L1 \times 100$$

where L1 is the length (in the direction for orientation) before shrinkage, and L2 is the length (in the direction for orientation) after shrinkage.

(7) Spontaneous shrinkability: An oriented film is left at stand at 30° C. for 30 days, whereupon the spontaneous shrinkability was calculated by the following formula:

$$\text{Spontaneous shrinkability (\%)} = (L3 - L4) / L3 \times 100$$

where L3 is the length (in the direction for orientation) before being left, and L4 is the length (in the direction for orientation) after being left.

Method for preparing block copolymers (I) P1 to P12 of Examples or Comparative Examples

Styrene and butadiene were polymerized in cyclohexane using n-butyl lithium as a polymerization initiator and tetrahydrofuran as a randomization agent, to obtain a block copolymer having structural characteristics as identified in Table 1, 2, 3 or 4. The number average molecular weight (Mn) was adjusted by the amount of n-butyl lithium, and the block proportion and the S1 to s3 chain proportion were adjusted by the amount of tetrahydrofuran. For example, block copolymer P1 was prepared as follows. Into a 100 l polymerization reactor, 65 l of cyclohexane, 7.8 g of tetrahydrofuran and 3.5 kg of styrene were charged, and 114 ml of n-butyl lithium (a 10% cyclohexane solution) was added thereto at a temperature of 30° C. with stirring. Then, the temperature was raised, and polymerization was carried out at a temperature of 45° C. for one hour. Then, 7.38 kg of styrene and 1.87 kg of butadiene were added, and polymerization was carried out at 70° C. for one hour. Then, 7.38 kg of styrene and 1.87 kg of butadiene were further added, and polymerization was carried out at 70° C. for one hour. Thereafter, an excess methanol was added to the polymer-

ization solution to terminate the polymerization, and the solvent was removed, followed by drying to obtain the desired block copolymer P1.

Further, block copolymer P4 was prepared as follows. Into a 100 l polymerization reactor, 65 l of cyclohexane, 7.8 g of tetrahydrofuran and 3.08 kg of styrene were charged, and 118 ml of n-butyl lithium (a 10% cyclohexane solution) was added thereto at a temperature of 30° C. with stirring. Then, the temperature was raised, and polymerization was carried out at a temperature of 45° C. for one hour. Then, 310 g of butadiene was added, and polymerization was carried out at 60° C. for one hour. Then, 7.92 kg of styrene and 1.23 kg of butadiene were added, and polymerization was carried out at 70° C. for one hour. Then, 310 g of butadiene was added, and polymerization was carried out at 70° C. for one hour. Then, 7.92 kg of styrene and 1.23 kg of butadiene were further added, and polymerization was carried out at 70° C. for one hour. Thereafter, the same operation as described above was carried out to obtain the desired block copolymer P4. The structural characteristics such as the number average molecular weight and the storage modulus ratio of the obtained copolymer are shown in Table 1, 2, 3 or 4.

#### EXAMPLES 1 TO 5 and COMPARATIVE EXAMPLES 1 TO 7

With respect to each block copolymer, the physical properties of an injection molded product and the heat shrinkability and spontaneous shrinkability of a film, are shown in Table 1, 2, 3 or 4. Whereas, the film was prepared by firstly extrusion molding a sheet having a thickness of 0.3 mm at a temperature of 210° C. and then transversely uniaxially orienting the sheet five times at 90° C. by means of a biaxial orientation apparatus manufactured by Kabushiki Kaisha Toyo Seiki Seisakusho (thickness: about 60 μm). This film was used as a test specimen for the tests of the above items (6) (heat shrinkability) to (7) (spontaneous shrinkability). From the physical properties shown in Tables 1 to 4, it is evident that the block copolymers of the present invention are excellent in transparency, stiffness, impact resistance and spontaneous shrinkage resistance.

TABLE 1

Type of block copolymer		Examples		
		1 P1	2 P2	3 P3
Structural characteristics	Weight ratio of styrene to butadiene (charged amounts)	83/17	83/17	83/17
	General formula	A-B-B	A-B-B	A-B-B
	Number average molecular weight (Mn)	184,000	204,000	188,000
	E'30/E'10	0.84	0.90	0.94
	Styrene block proportion (%)	81	80	82
Physical properties	s1 to s3 chain proportion (%)	16	16	13
	Haze (%)	1.5	1.5	1.6
	Tensile modulus (kg/cm <sup>2</sup> )	12,300	12,600	13,100
	Izod impact strength	2.2	2.2	2.3

TABLE 1-continued

Type of block copolymer	Examples		
	1 P1	2 P2	3 P3
(kg · cm/cm)			
Heat shrinkability (%)	49	41	43
Spontaneous shrinkability (%)	2.1	2.0	1.4

TABLE 2

Type of block copolymer		Examples	
		4 P4	5 P5
Structural characteristics	Weight ratio of styrene to butadiene (charged amounts)	86/14	75/25
	General formula	A-C-B-C-B	A-C-B-C-B-B
	Number average molecular weight (Mn)	178,000	212,000
	E'30/E'10	0.92	0.81
	Styrene block proportion (%)	83	78
	s1 to s3 chain proportion (%)	12	18
Physical properties	Haze (%)	1.3	2.0
	Tensile modulus (kg/cm <sup>2</sup> )	14,600	11,300
	Izod impact strength (kg · cm/cm)	2.2	2.9
	Heat shrinkability (%)	45	42
	Spontaneous shrinkability (%)	1.6	2.2

TABLE 3

Type of block copolymer		Comparative Examples			
		1 P6	2 P7	3 P8	4 P9
Structural characteristics	Weight ratio of styrene to butadiene (charged amounts)	56/46	95/5	79/21	81/19
	General formula	A-B-B	A-B-B	A-B-B	A-B-B
	Number average molecular weight (Mn)	162,000	185,000	30,000	192,000
	E'30/E'10	0.81	0.97	0.87	0.73
	Styrene block proportion (%)	70	93	83	72
	s1 to s3 chain proportion (%)	19	5	13	21
Physical properties	Haze (%)	4.6	0.8	2.5	2.0
	Tensile modulus (kg/cm <sup>2</sup> )	6,900	19,500	9,700	12,200
	Izod impact strength (kg · cm/cm)	4.3	1.1	1.4	2.2

TABLE 3-continued

Type of block copolymer		Comparative Examples			
		1 P6	2 P7	3 P8	4 P9
Heat shrinkability (%)		41	Too brittle to form a film	35	44
Spontaneous shrinkability (%)		3.6		0.9	3.2

TABLE 4

Type of block copolymer		Comparative Examples		
		5 P10	6 P11	7 P12
Structural characteristics	Weight ratio of styrene to butadiene (charged amounts)	73/27	82/18	80/20
	General formula	A-B-B	A-B-B	A-B-B
	Number average molecular weight (Mn)	80,000	186,000	520,000
	E'30/E'10	0.76	0.76	0.83
	Styrene block proportion (%)	65	71	79
	s1 to s3 chain proportion (%)	23	26	19
Physical properties	Haze (%)	4.2	2.1	2.9
	Tensile modulus (kg/cm <sup>2</sup> )	9,800	11,800	13,600
	Izod impact strength (kg · cm/cm)	3.4	2.2	2.7
	Heat shrinkability (%)	41	43	Impossible to form a proper sheet
	Spontaneous shrinkability (%)	2.8	3.4	

Now, Examples for the block copolymer composition of the present invention will be described. The measurements of the physical properties of each block copolymer composition, were carried out in the same manner as for the above described block copolymer. The film was prepared by firstly extrusion molding a sheet in the same manner as above and then transversely uniaxially orienting the sheet five times at 95° C. (thickness: about 60 μm).

#### EXAMPLES 6 TO 11 and COMPARATIVE EXAMPLES 8 TO 17

Using the polymer as identified in Table 5 as the polymer (II), a block copolymer composition was prepared in accordance with the blend formulation as identified in Table 6 or 7. With respect to each block copolymer composition, the

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		Examples							
		6	7	8	9	10	11		
<b>Blend properties</b>	Type and amount of block copolymer	P1 80	P1 85	P1 99	P1 90	P1 60	P4 80		
	Type and amount of blend polymer	a 20	b 15	c 1	e 9	a 33	d 20		
	(parts by weight)				e 1	b 5			
							e 2		
<b>Physical properties</b>	Haze (%)	1.6	1.7	3.1	3.2	4.6	1.5		
	Tensile modulus (kg/cm <sup>2</sup> )	12,200	14,500	12,600	14,000	13,200	16,800		
	Izod impact strength (kg · cm/cm)	2.3	2.0	2.4	2.1	2.4	2.1		
	Heat shrinkability (%)	45	41	43	42	43	42		
	Spontaneous shrinkability (%)	2.3	1.6	2.2	1.7	1.8	1.1		

TABLE 7

		Comparative Examples									
		8		9		10		11		12	
Blend	Type and amount (parts by weight) of block copolymer	P6	85	P7	85	P8	85	P9	85	P10	85
	Type and amount (parts by weight) of blend polymer	b	15	b	15	b	15	b	15	b	15
Physical properties	Haze (%)	4.7		0.9		2.7		2.2		4.4	
	Tensile modulus (kg/cm <sup>2</sup> )	9,500		21,000		11,000		14,400		12,300	
	Izod impact strength (kg · cm/cm)	3.5		1.0		1.1		1.9		3.0	
	Heat shrinkability (%)	41		Too brittle to form a film		33		42		40	
	Spontaneous shrinkability (%)	3.0				0.7		2.8		2.7	
		Comparative Examples									
		13		14		15		16		17	
Blend	Type and amount (parts by weight) of block copolymer	P11	85	P12	85	P1	4	P1	25	P1	60
	Type and amount (parts by weight) of blend polymer	b	15	b	15	a	96	c	75	d e	10 30
Physical properties	Haze (%)	2.2		3.2		1.7		1.9		90	
	Tensile modulus (kg/cm <sup>2</sup> )	14,000		15,600		11,600		24,200		15,700	
	Izod impact strength (kg · cm/cm)	2.0		2.4		2.4		1.2		4.2	
	Heat shrinkability (%)	40		Impossible to form a proper sheet		47		Too brittle to form a film		38	
	Spontaneous shrinkability (%)	2.9				3.0				1.2	

A heat shrinkable film obtained by orienting the block copolymer of the present invention or a composition of the block copolymer, is excellent in transparency, stiffness, impact resistance and spontaneous shrinkage resistance and thus is suitable for covering an article which is likely to scatter upon breakage, such as a glass bottle, or as a heat shrinkable film for labels provided with various printings. Further, the block copolymer and the block copolymer composition of the present invention may be molded by injection molding or blow molding to obtain various molded products, or they may be formed into films or sheets by e.g. extrusion molding or inflation molding and may be used as they are, or may further be subjected to secondary processing such as vacuum forming for various applications.

What is claimed is:

1. A block copolymer (I) consisting essentially of a vinyl aromatic hydrocarbon and a conjugated diene and satisfying the following conditions (1) to (5):

- (1) the weight ratio of vinyl aromatic hydrocarbon units to conjugated diene units is from 60:40 to 90:10,
- (2) the number average molecular weight of the block copolymer is from 40,000 to 500,000,
- (3) the ratio of E'30/E'10, where E'30 is the storage modulus at a temperature of 30° C. and E'10 is the storage modulus at a temperature of 10° C., is from 0.75 to 1,
- (4) the homopolymer block proportion of a vinyl aromatic hydrocarbon polymer contained in the block copolymer is from 70 to 100%, provided the block proportion=

W1/W0×100, where W1 is the weight of homopolymer block polymer chains of the vinyl aromatic hydrocarbon in the block copolymer, and W0 is the total weight of the vinyl aromatic hydrocarbon units in the block copolymer, and

(5) chains consisting of from 1 to 3 repeating units of the vinyl aromatic hydrocarbon contained in the block copolymer, are not more than 25%, based on the above W0.

2. The block copolymer according to claim 1, wherein the structure of the block copolymer (I) is represented by one of the following formulae:

- (a) A—(B)<sub>m</sub>
- (b) A—C—(B)<sub>m</sub>
- (c) A—(C—B)<sub>m</sub>
- (d) A—(C—B)<sub>m</sub>—(B)<sub>n</sub>

where A is a polymer chain of the vinyl aromatic hydrocarbon, B is a copolymer chain of the vinyl aromatic hydrocarbon and the conjugated diene, C is a polymer chain of the conjugated diene, m is an integer of at least 2, and n is an integer of at least 1.

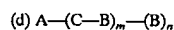
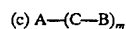
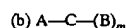
3. A heat shrinkable film made of the block copolymer as defined in claim 1.

4. A block copolymer composition comprising the block copolymer (I) as defined in claim 1 and the following polymer (II):

(II) at least one polymer selected from the group consisting of (i) a block copolymer consisting essentially of a vinyl aromatic hydrocarbon and a conjugated diene, which is different from the block copolymer (I) as defined in claim 1, (ii) a vinyl aromatic hydrocarbon polymer, (iii) a copolymer consisting essentially of a vinyl aromatic hydrocarbon and a (meth)acrylate, and (iv) a rubber-modified styrene type polymer.

5. The block copolymer composition according to claim 4, which comprises from 50 to 99.8 parts by weight of the block copolymer (I) and from 0.2 to 50 parts by weight of the polymer (II), provided that the total amount of the polymers (I) and (II) is 100 parts by weight, and when the polymer (II) is the rubber-modified styrene type polymer (iv), the amount of the polymer (iv) is not more than 20 parts by weight.

6. The block copolymer composition according to claim 4, wherein the structure of the block copolymer (I) is represented by one of the following formulae:



where A is a polymer chain of the vinyl aromatic hydrocarbon, B is a copolymer chain of the vinyl aromatic hydrocarbon and the conjugated diene, C is a polymer chain of the conjugated diene, m is an integer of at least 2, and n is an integer of at least 1.

7. A heat shrinkable film made of a block copolymer composition as defined in claim 4.

\* \* \* \* \*



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(12) **United States Patent**  
Matsui et al.

(10) **Patent No.:** US 6,841,261 B2  
(45) **Date of Patent:** Jan. 11, 2005

(54) **BLOCK COPOLYMER, COMPOSITION THEREOF, AND FILM MADE THEREOF**

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Mar. 22, 2001	(JP)	2001-082539
Sep. 19, 2001	(JP)	2001-284430
Oct. 16, 2001	(JP)	2001-317984

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(56) **References Cited**

**U.S. PATENT DOCUMENTS**

3,872,068 A 3/1975 Horie et al.

4,089,913 A *	5/1978	Miki et al.	525/272
4,386,125 A	5/1983	Shiraki et al.	
4,987,194 A *	1/1991	Maeda et al.	525/314
5,583,182 A	12/1996	Asahara et al.	
5,756,577 A	5/1998	Gutierrez-Villarreal	
6,107,411 A *	8/2000	Toya et al.	525/316
2003/0158336 A1 *	8/2003	Yaguchi et al.	525/95
2004/0072957 A1 *	4/2004	Terano et al.	525/323
2004/0097658 A1 *	5/2004	Everaerts et al.	525/244
2004/0102576 A1 *	5/2004	Matsui et al.	525/180

#### FOREIGN PATENT DOCUMENTS

EP	0 362 850	4/1990
EP	0 852 240	7/1998
GB	1 422 030	1/1976
GB	2 245 574	1/1992
JP	60-097827	5/1985
JP	60-099116	6/1985
WO	WO 91/13935	9/1991

#### OTHER PUBLICATIONS

Patent Abstracts of Japan, JP 07-216186, Aug. 15, 1995.  
Patent Abstracts of Japan, JP 11-228783, Aug. 24, 1999.  
Patent Abstracts of Japan, JP 07-097419, Apr. 11, 1995.  
Patent Abstracts of Japan, JP 02-222440, Sep. 5, 1990.

\* cited by examiner

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(57) **ABSTRACT**

It is to provide a block copolymer and its copolymer composition which provides a heat shrinkable (multilayer) film with less spontaneous shrinkage while maintaining favorable low temperature shrinkability, and a heat shrinkable (multilayer) film containing the block copolymer. By using a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene characterized in that the relation of the loss tangent value obtained by dynamic viscoelasticity measurement with the temperature satisfies specific conditions, or a composition containing the copolymer composition as an essential component, a heat shrinkable (multilayer) film with less spontaneous shrinkability and less odor while maintaining favorable low temperature shrinkability can be obtained.

**51 Claims, No Drawings**



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# BLOCK COPOLYMER, COMPOSITION THEREOF, AND FILM MADE THEREOF

## TECHNICAL FIELD

The present invention relates to a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene, having favorable transparency and impact resistance, and being excellent in film formability into a sheet or a film, and a resin composition containing it. Particularly, it relates to a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, useful as a material for production of a heat shrinkable film, which has favorable shrinkability when used as a heat shrinkable film and which has low properties such that the heat shrinkable film slightly shrinks at a temperature of the shrinkage initiation temperature or under (hereinafter referred to as "spontaneous shrinkage") as compared with a conventional one, whereby shearing or distortion of printing caused by the spontaneous shrinkage or wrinkles at the time of shrinkage may further be suppressed, a polymer composition composed mainly of it, and a heat shrinkable (multilayer) film composed mainly of such a block copolymer and/or another polymer composition.

In the present invention, a membrane-like body having a thickness of at most 0.2 mm is referred to as a film, and one having a thickness exceeding 0.2 mm is referred to as a sheet.

## BACKGROUND ART

It is known that when a vinyl aromatic hydrocarbon and a conjugated diene are subjected to block copolymerization by living anionic polymerization in an organic solvent using an alkyl lithium as an initiator, the structure of the copolymer can be diversified by a method of e.g. changing the weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene or changing the manner of addition, whereby block copolymers having various physical properties can be obtained. In general, a block copolymer is a polymer having excellent impact resistance and transparency. If the content of the conjugated diene in the block copolymer is large, the copolymer tends to be a thermoplastic elastomer. On the other hand, if the content of the vinyl aromatic hydrocarbon is large, the copolymer tends to show characteristics as thermoplastics. To utilize such excellent characteristics, various production methods have been disclosed, for example, in JP-B-36-19286 and JP-B-48-4106.

The block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene produced by these methods has a high transparency and favorable moldability, and therefore as disclosed in JP-B-63-49702, a heat shrinkable film having such characteristics that it shrinks in a short time at a temperature of at least the shrinkage initiation temperature, while it keeps the original shape at room temperature, can be obtained by using the resin as a raw material. This heat shrinkable film is produced by carrying out a processing operation wherein the resin extruded into a plate shape or a tube shape at a temperature of at least the softening point of the resin is oriented in a uniaxial or a biaxial direction to obtain a film, which is directly cooled to room temperature. By carrying out the series of processing operation including orienting, an individual molecule constituting the film is fixed as aligned in a specific direction, whereby the internal stress remains, and the heat shrinkable film is a film utilizing the shrinking phenomenon caused by that the above-described residual stress is relieved by re-heating.

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Further, in addition to these excellent properties, it is excellent in miscibility with various vinyl aromatic hydrocarbon polymers, and it is thereby used for reinforcement, which is disclosed, for example, in JP-B-45-19388, JP-B-47-43618 and JP-B-51-27701. However, such block copolymers and compositions are relatively transparent, have favorable impact resistance and their oriented films show heat shrinkability, whereby they are favorably employed as various heat shrinkable packaging materials and labeling materials for beverage bottles on which tradenames and the like are printed. Particularly with respect to shrinkable labeling materials, as a result of increase in demand for plastic bottle beverages in recent years, line speed in a labeling step has been increased year by year, and reduction of time required for labeling and shrinkage has been attempted, and accordingly a film which requires a short time for heating, i.e. a film which shrinks at a low temperature, has been desired. However, a conventional film for shrink labels has a high heat shrinkage initiation temperature, and shrinkage at a relatively high temperature is required so as to obtain favorable shrinkage finish.

Further, if the molecular structure or the composition formulation is set so that the film starts to shrink at a low temperature merely by a conventional method, the heat shrinkable film shrinks during storage (so-called spontaneous shrinkage), thus causing printing slippage or labeling failure. As mentioned above, with respect to a film obtained by a conventional technique, no material having a balance among low temperature shrinkability and spontaneous shrinkage resistance, and outer appearance after shrinkage, has been obtained, and further, surface roughening may form on the film surface, thus impairing the outer appearance, in some cases. In JP-A-59-221348 and Japanese Patent No. 3,026,497, it has been studied to blend a styrene-acrylate type resin to obtain a multilayer film, from the viewpoint of reduction of spontaneous shrinkage and improvement in low temperature shrinkability of a styrene-butadiene block copolymer. However, it is not satisfactory from the viewpoint of e.g. needs for low temperature shrinkability in recent years and odor, and further, width of conditions at the time of orienting the film tends to be narrow, such being unsatisfactory.

It is an object of the present invention to provide a copolymer and its composition, capable of forming a film which satisfies needs such as low temperature shrinkability in recent years, spontaneous shrinkage resistance and reduction of odor, and which is excellent in outer appearance, for application as e.g. a heat shrinkable film, and a heat shrinkable film and a heat shrinkable multilayer film made of said copolymer or its composition.

## DISCLOSURE OF THE INVENTION

Under these circumstances, in order to overcome the above problems, the present inventors have conducted detailed and extensive studies on a block copolymer and a composition comprising it, suitable as a raw material of a heat shrinkable film capable of forming an oriented film, which provides less odor, which has favorable low temperature shrinkability, which is less likely to undergo spontaneous shrinkage, and which is excellent in outer appearance. As a result, they have found that the above problems can be overcome by blending a block copolymer which satisfies a specific condition of the dynamic viscoelasticity characteristics, particularly the temperature dependency of the loss tangent value which shows a state of the block copolymer becoming softened. The present invention has been accomplished on the basis of this discovery.

The present invention may be classified into a block copolymer (A) according to claims 1 to 4 and a composition containing at least two types of the different block copolymers (A) according to claims 5 to 7 as a first invention, a composition containing the block copolymer (A) and a vinyl aromatic hydrocarbon polymer according to claims 8 and 9 as a second invention, a composition containing the block copolymer (A) and a block copolymer (A2) according to claims 10 to 13 as a third invention, a composition containing the block copolymer (A) and a block copolymer (A3) according to claims 14 to 17 as a fourth invention, a film or sheet made of the block copolymer (A) or the composition according to claims 18 to 31 as a fifth invention, and a method for producing the block copolymer (A) according to claims 32 and 33 as a sixth invention.

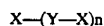
First, the block copolymer (A) and the composition containing at least two types of the different block copolymers (A) as the first invention will be explained below.

The block copolymer (A) of the present invention is a block copolymer (A) comprising a vinyl aromatic hydrocarbon and a conjugated diene, wherein the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature satisfies (1) there is at least one maximum value within a temperature range of from 60 to 110° C., (2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and (3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value.

Further, in the relation of the loss tangent value obtained by dynamic viscoelasticity measurement of the block copolymer (A) to the temperature, the highest maximum value of the loss tangent value in a temperature range of from 60 to 110° C. is preferably within a range of from 0.5 to 4.0, and the loss tangent value at 30° C. is preferably within a range of at least 0.01 and less than 0.4.

The weight average molecular weight (Mw) of the block copolymer (A) of the first invention as measured by gel permeation chromatography (GPC) is preferably within a range of  $100,000 \leq Mw \leq 300,000$ , more preferably  $120,000 \leq Mw \leq 250,000$ , most preferably  $150,000 \leq Mw \leq 220,000$ . If Mw is less than 100,000, strength of the obtained copolymer may not be satisfactory for practical use in some cases, and if it exceeds 300,000, the great force tends to be required when it is formed into a sheet or film, and it tends to be somewhat difficult to obtain a favorable product.

Further, it is preferred that the molecular structure of the block copolymer (A) is represented by the following formula, its weight average molecular weight is from 100,000 to 300,000, and conditions (a) to (c) are satisfied:



wherein n is an integer of at least 1:

- (a) X is a block having a chain comprising one type or at least two types of vinyl aromatic hydrocarbons,
- (b) Y is a block containing at least one random copolymer segment of a conjugated diene and a vinyl aromatic hydrocarbon, each being of one type or at least two types, having a weight average molecular weight of from 40,000 to 250,000, and
- (c) when a molecular weight distribution of a polymer mixture comprising a vinyl aromatic hydrocarbon obtained by ozonolysis of the block copolymer is measured, the relation between the weight average

molecular weight (Mw') of the polymer component showing the highest peak and the weight average molecular weight (Mw) of the block copolymer before the treatment is  $0.1 \leq Mw'/Mw \leq 0.4$ .

Block X may be obtained by polymerizing one type or at least two types of vinyl aromatic hydrocarbons, and it may be either a polymer block comprising a single vinyl aromatic hydrocarbon or a copolymer block comprising a plurality of vinyl aromatic hydrocarbons. Further, the structures, the compositions and the molecular weights of the plurality of blocks X, may be the same or different. The weight ratio of the block based on the whole is not limited, but it is preferably at least 2 wt % so as to later obtain strength as a molded product such as a film.

Block Y is obtained by polymerizing a conjugated diene and a vinyl aromatic hydrocarbon, each being of one type or at least two types. With respect to block Y also, in a case where n in the molecular structural formula  $X-(Y-X)_n$  is at least 1, and a plurality of blocks Y is present, their structures, compositions and the molecular weights may be the same or different in the same manner as block X.

Copolymer block Y is required to contain at least one random copolymer segment of a vinyl aromatic hydrocarbon and a conjugated diene, having a weight average molecular weight of from 40,000 to 250,000. If it is at most 40,000, no balance between favorable heat shrinkability and spontaneous shrinkage will be obtained, and if it is at least 250,000, film formability tends to decrease, such being unfavorable. The weight average molecular weight of the random copolymer segment can be obtained in such a manner that each monomer is added in the polymerization step, and a small amount of the copolymer solution is taken out from the polymerization reactor before and after the step of completely polymerizing the monomers, and the solutions are subjected to molecular weight measurement by means of a gel permeation chromatography (hereinafter referred to as GPC measurement), and the weight average molecular weights are compared.

Further, in GPC measurement of the vinyl aromatic hydrocarbon polymer components obtained by ozonolysis of the block copolymer of the present invention, the relation of  $0.1 \leq Mw'/Mw \leq 0.4$  is built up between the weight average molecular weight (Mw') corresponding to the highest peak of the molecular weight distribution curve and the weight average molecular weight (Mw) of the entire block copolymer. Namely, the ratio of the weight average molecular weight of the highest component among the vinyl aromatic hydrocarbon polymer components to the weight average molecular weight of the entire block copolymer is at least 0.1 and at most 0.4, preferably at least 0.2 and at most 0.35. If it is less than 0.1, film formability tends to decrease, and if it exceeds 0.4, heat shrinkability tends to decrease, and thus the effect of the present invention can hardly be obtained.

In the molecular structure of  $X-(Y-X)_n$  of the present invention, block X comprising the vinyl aromatic hydrocarbon at each terminal functions as a physical crosslinking point between molecules, such being preferred in view of appearance of strength as the resin molded product. Further, block Y in the middle is characterized by containing at least one random copolymer segment comprising a vinyl aromatic hydrocarbon and a conjugated diene. By the presence of this segment, heat shrinkability and spontaneous shrinkage resistance can be well balanced. Further, with a purpose of further imparting "elongation" property and flexibility of the film, a chain comprising a conjugated diene may further be added to Y.

The weight average molecular weight of the conjugated diene polymer block in block Y can be obtained in such a manner that the conjugated diene monomer is added in a polymerization step, a small amount of the copolymer solution is taken out from the polymerization reactor before and after the step of completely polymerizing the monomer, and the solutions are subjected to GPC measurement, and the weight average molecular weights are compared.

The composition of the first invention is a block copolymer composition containing at least two types of the different block copolymers (A).

It is preferably a block copolymer composition wherein the relation of the loss tangent value obtained by dynamic viscoelasticity measurement of the composition to the temperature satisfies conditions (1) there is at least one maximum value within a temperature range of from 60 to 110° C., (2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and (3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value.

Now, the composition containing the block copolymer (A) and a vinyl aromatic hydrocarbon polymer according to the second invention will be explained below.

The composition is a composition containing the block copolymer (A) comprising a vinyl aromatic hydrocarbon and a conjugated diene and at least one member selected from the following vinyl aromatic hydrocarbon polymers (B1) to (B3):

- (B1) a vinyl aromatic hydrocarbon polymer,
- (B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A)), and
- (B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

The vinyl aromatic hydrocarbon polymers (B1) to (B3) will be explained hereinafter.

Now, the composition containing the block copolymer (A) and a block copolymer (A2) according to the third invention will be explained below.

Of the composition, the compositional ratio by weight of the block copolymer (A) to the following block copolymer (A2) is required to be within a range of  $0.1 \leq A/(A+A2) \leq 0.95$ .

The block copolymer (A2) is a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene, wherein in the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, there is at least one maximum value within a temperature range of from 63 to 120° C., and the lowest temperature for the maximum value of the loss tangent value within said range is higher by at least 3° C. than the lowest temperature for the maximum value of the loss tangent value of the block copolymer (A).

Particularly preferred is a copolymer composition comprising the block copolymer (A) and the block copolymer (A2), wherein in the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the

temperature of the block copolymer (A2), the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value of the loss tangent value within a range of from 63 to 120° C., is at most 40% of the maximum value, and the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the maximum value.

Further, the composition according to the third invention may contain at most 100 parts by weight of at least one vinyl aromatic hydrocarbon resin selected from the following polymers (B1) to (B3) based on 100 parts by weight of the above copolymer composition comprising (A) and (A2):

- (B1) a vinyl aromatic hydrocarbon polymer,
- (B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A) and the block copolymer (A2)),
- (B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

The compositional ratio of the vinyl aromatic hydrocarbon and the conjugated diene in the block copolymers (A) and (A2) is not particularly limited, however, the weight ratio of the conjugated diene is preferably within a range of at least 5% and less than 40%, more preferably within a range of from 7% to 30%. The molecular weight is not particularly limited also, however, the weight average molecular weight by gel permeation chromatography (as calculated as polystyrene) is preferably at least 50,000 and less than 500,000, more preferably at least 100,000 and less than 300,000.

Now, the block copolymer (A2) of a vinyl aromatic hydrocarbon and a conjugated diene will be explained. This block copolymer is characterized by that in a relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, there is at least one maximum value within a range of from 63 to 120° C., and the lowest temperature for the maximum value of the loss tangent value within said range is a temperature higher by at least 3° C., preferably by at least 5° C., more preferably by at least 10° C. and at most 30° C., than the lowest temperature for the maximum value of the loss tangent value as defined in the item for the block copolymer (A). By mixing the block copolymer (A2) of a vinyl aromatic hydrocarbon and a conjugated diene having such characteristics with the block copolymer (A), a resin composition excellent in processing properties such that it emits less odor, it is excellent in spontaneous shrinkage resistance and low temperature shrinkability, and the range of conditions particularly for orienting can be widened, can be obtained.

The block copolymer (A2) particularly preferably has a relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature such that the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value among maximum values within a temperature range of from 63 to 120° C., is at most 40% of the maximum value, and the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the maximum value, in view of spontaneous shrinkage resistance. The block copolymer having such characteristics can be produced in

the same method as for the block copolymer (A) as mentioned hereinafter. The maximum value of the loss tangent value obtained by dynamic viscoelasticity measurement can be controlled by optionally changing the weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene at the segment portion of the copolymer chain of the vinyl aromatic hydrocarbon and the conjugated diene.

In the third invention, the compositional ratio by weight of the block copolymer (A) to the block copolymer (A2) is within a range of  $0.1 \leq A/(A+A2) \leq 0.95$ , preferably  $0.3 \leq A/(A+A2) \leq 0.9$ , particularly preferably  $0.5 \leq A/(A+A2) \leq 0.8$ . By mixing such a polymer having a special relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, a copolymer composition excellent in processing properties such that it emits less odor, it is excellent in low temperature shrinkability and spontaneous shrinkage resistance, and the range of orienting conditions particularly when formed into a shrinkable film can be widened, can be obtained.

Further, it is preferred that the block copolymer (A) or (A2) has a block portion corresponding to a maximum value of the loss tangent value of at 0° C. or below, in order to increase impact resistance of a (multilayer) sheet, (multilayer) film or heat shrinkable (multilayer) film obtained by using the copolymer composition containing the block copolymers (A) and (A2) as essential components.

In the third invention, the amount of the vinyl aromatic hydrocarbon polymers (B1) to (B3) is such that the vinyl aromatic hydrocarbon polymer is at most 100 parts by weight, preferably at most 75 parts by weight, particularly preferably at most 50 parts by weight, based on 100 parts by weight of the copolymer composition comprising (A) and (A2). If it exceeds 100 parts by weight, at least one characteristics of the obtained heat shrinkable (multilayer) film among spontaneous shrinkage resistance, low temperature shrinkability, impact resistance and transparency tends to be impaired.

Now, the composition containing the block copolymer (A) and a block copolymer (A3) according to the fourth invention will be explained.

The composition is a composition comprising the block copolymer (A) having a weight average molecular weight  $Mw1$  within a range of  $100,000 \leq Mw1 \leq 300,000$ , and a block copolymer (A3) comprising a vinyl aromatic hydrocarbon and a conjugated diene and having a weight average molecular weight  $Mw2$  in relation to  $Mw1$  within a range of  $0.1 \leq Mw2/Mw1 \leq 0.85$ , wherein the compositional ratio by weight of (A) to (A3) is within a range of  $0.1 \leq A/(A+A3) \leq 0.9$ .

Further, it may be a copolymer composition which contains at most 100 parts by weight of a vinyl aromatic hydrocarbon polymer containing at least one of the following (B1) to (B3) based on 100 parts by weight of the copolymer composition:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A)),

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

The compositional ratio of the vinyl aromatic hydrocarbon and the conjugated diene contained in each of the block copolymers (A) and (A3) is not particularly limited, however, the weight ratio of the conjugated diene is preferably at least 5% and less than 50%, and more preferably within a range of from 7% to 40%. Further, when (A) and (A3) are mixed to obtain a composition, the weight ratio of the conjugated diene based on the entire composition is preferably at least 7% and less than 35%, more preferably at least 12% and less than 25%.

Further, the block copolymer (A3) according to the fourth invention has a weight average molecular weight ( $Mw2$ ) by gel permeation chromatography (GPC) measurement in relation to the weight average molecular weight  $Mw1$  of the block copolymer (A) within a range of  $0.1 \leq Mw2/Mw1 \leq 0.85$ , preferably  $0.3 \leq Mw2/Mw1 \leq 0.80$ , more preferably  $0.4 \leq Mw2/Mw1 \leq 0.75$ , most preferably  $0.5 \leq Mw2/Mw1 \leq 0.72$ . If  $Mw2/Mw1$  is less than 0.1, the strength of the obtained film tends to be low, and if it exceeds 0.85, the surface of the obtained oriented film may be wrinkled or surface roughening may occur.

The copolymer composition composed mainly of a block copolymers (A) and (A3) of a vinyl aromatic hydrocarbon and a conjugated diene is preferably such that in the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, the loss tangent value has at least one maximum value within a temperature range of from 60 to 110° C., more preferably from 60 to 100° C., furthermore preferably from 75 to 90° C., the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value of the loss tangent value within said range, is at most 40% of the highest value, and the value of loss tangent at a temperature lower by 30° C. is at most 10% of the highest value. By such characteristics, favorable spontaneous shrinkage resistance and low temperature shrinkability can be imparted.

In the fourth invention, it is required that the compositional ratio by weight of the block copolymer (A) to the block copolymer (A3) is within a range of  $0.1 \leq A/(A+A3) \leq 0.9$ , preferably  $0.2 \leq A/(A+A3) \leq 0.8$ . If the compositional ratio is out of this range, characteristics of each component can not adequately be made use of, and film formation properties tend to decrease, and outer appearance of the sheet or film may be impaired, or shrinkage properties of the oriented film tends to deteriorate in some cases. By mixing such a polymer having a specific molecular weight and having a special relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, a copolymer composition excellent in processing properties such that it emits less odor, it is excellence in low temperature shrinkability and spontaneous shrinkage resistance, and the range of orienting conditions particularly when formed into a shrinkable film can be widened, can be obtained.

The fifth invention relates to a film, a sheet or a heat shrinkable film made of the block copolymer (A) or a copolymer composition comprising it, and a multilayer film, a multilayer sheet or a heat shrinkable multilayer film employing the block copolymer (A) or a copolymer composition comprising it for at least one layer.

Further, the sixth invention of the present invention relates to a method for producing the block copolymer (A).

#### BEST MODE FOR CARRYING OUT THE INVENTION

Now, the present invention will further be explained additionally and in detail.

A chemical structure of each of the block copolymers (A), (A2) and (A3) of a vinyl aromatic hydrocarbon and a

conjugated diene of the present invention is not particularly limited, and the polymer may have a block copolymer structure wherein the vinyl aromatic hydrocarbon chain and the conjugated diene chain are separated, or the vinyl aromatic hydrocarbon and the conjugated diene may be bonded to each other randomly or with a low rate of change of concentration gradient. Further, it is preferably a block copolymer having a vinyl aromatic chain at least one terminal, particularly preferably at each terminal, so as to achieve favorable heat stability at the time of processing.

The loss tangent value obtained by dynamic viscoelasticity measurement of the present invention is represented as a value of the ratio of loss elasticity modulus obtained as a response when a stress and strain in a tensile direction repeated in a sine wave are imparted to a test material, to the storage elasticity modulus. It means the bound state of molecules in the test specimen, and a high loss tangent value means that molecules are more likely to be loosely bonded, and the heat shrinkable film is more likely to shrink at the temperature. The value obtained by dynamic viscoelasticity varies depending upon the measurement method and conditions, and in the present invention, a sheet having a thickness of from 0.1 to 0.5 mm is subjected to solid viscoelasticity measurement at a measurement temperature within a range of from room temperature to 120° C., at a temperature-raising rate of 4° C./min at a measurement frequency of 1 Hz.

As the vinyl aromatic hydrocarbon used in each of the block copolymers (A), (A2) and (A3) comprising a vinyl aromatic hydrocarbon and a conjugated diene, styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene,  $\alpha$ -methylstyrene, vinyl naphthalene or vinyl anthracene may, for example, be mentioned, and particularly preferably styrene may be mentioned.

Further, the conjugated diene may, for example, be 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene or 1,3-hexadiene, and particularly preferably 1,3-butadiene or isoprene may be mentioned.

A compositional ratio of the vinyl aromatic hydrocarbon and the conjugated diene in the block copolymer (A) in the present invention is not particularly limited, however, the weight ratio of the conjugated diene is preferably within a range of from 5 to 40%, more preferably from 7 to 30%.

The molecular weight of the block copolymer (A) is not particularly limited also, however, the weight average molecular weight is preferably at least 50,000 and less than 500,000, more preferably at least 100,000 and at most 300,000 as measured by gel permeation chromatography (as calculated as polystyrene). If the weight average molecular weight is less than 50,000, strength of the obtained copolymer tends to be inadequate, and if it exceeds 500,000, a great force will be required when it is processed into a sheet or film, and no favorable product tends to be obtained.

Each of the block copolymers (A), (A2) and (A3) of the present invention can be produced by blending the above explained vinyl aromatic hydrocarbon and conjugated diene, each being of one type or at least two types, and subjecting them to living anionic polymerization employing an organic lithium compound as a polymerization initiator in an organic solvent.

By the living anionic polymerization, polymerization of the vinyl aromatic hydrocarbon and conjugated diene as the material monomers continues so long as a polymerizable active terminal is present, whereby remaining of the mono-

mers can be suppressed. Further, there are such characteristics in view of polymerization reaction that the reactive active terminals are less likely to be deactivated and less likely to be newly formed during the polymerization by a chain transfer reaction. Accordingly, the molecular weight and the molecular structure of the copolymer in the present invention can be controlled depending upon the purpose, by optionally changing the charge amount, the timing of addition and the number of addition of the monomers, the polymerization initiator, the randomizing agent, and the proton donating substance used for deactivation of active terminals (hereinafter referred to as "polymerization terminator").

For example, in a case where a molecular structure of a block type wherein a chain of the vinyl aromatic hydrocarbon and a chain of the conjugated diene are separated is introduced, material chargings of the vinyl aromatic hydrocarbon and the conjugated diene are separately carried out, and after one reaction is completed, the next charging is carried out.

Further, to prepare a chain having a random structure, a randomizing agent which makes the reactivity ratios of the vinyl aromatic hydrocarbon and the conjugated diene same is selected and added, or each of the monomers is added little by little so that the feed weight of each monomer to the reaction system will be always slower than the reaction rate, that is, the reactive terminal of the polymer is always in a starved state.

Further, when the vinyl aromatic hydrocarbon and the conjugated diene are added to the reaction system simultaneously in the presence of a proper randomizing agent, a copolymer having a graded chain structure will be formed.

In the present invention, the randomizing agent is a molecule having polarity, and an amine, an ether, a thioether, and phosphoramidate, an alkyl benzene sulfonate, and an alkoxide of potassium or sodium may, for example, be used. As a suitable amine, a tertiary amine such as trimethylamine, triethylamine or tetramethylethylenediamine, or a cyclic tertiary amine may, for example, be used. The ether may, for example, be dimethyl ether, diethyl ether, diphenyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether or tetrahydrofuran. Further, triphenylphosphine, hexamethylphosphoramide, potassium alkyl benzene sulfonate or butoxide of e.g. sodium, potassium or sodium may, for example, be mentioned.

As the randomizing agent, one type or a plural types thereof may be used, and the concentration is suitably from 0.001 to 10 parts by weight in total based on 100 parts by weight of the material monomers.

As the organic solvent, an aliphatic hydrocarbon such as butane, pentane, hexane, isopentane, heptane, octane or isooctane, an alicyclic hydrocarbon such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane or ethylcyclohexane, or an aromatic hydrocarbon such as benzene, toluene, ethylbenzene or xylene, may, for example, be used.

The organic lithium compound as the polymerization initiator is a compound having at least one lithium atom bonded in its molecule, and in the present invention, a monofunctional polymerization initiator such as ethyl lithium, n-propyl lithium, isopropyl lithium, n-butyllithium, sec-butyllithium or tert-butyllithium, or a multifunctional polymerization initiator such as hexamethylene dilithium, butadienyl dilithium or isoprenyl dilithium may, for example, be used.

As the polymerization terminator in the living anionic polymerization in the present invention, at least one member selected from water, an alcohol, an inorganic acid, an organic acid and a phenol compound is added to the reaction system to terminate the polymerization.

As the polymerization terminator, water is particularly preferred.

The alcohol as the polymerization terminator may, for example, be methanol, ethanol or butanol, the inorganic acid may, for example, be hydrochloric acid, sulfuric acid, nitric acid, boric acid, phosphoric acid or carbonic acid, the organic acid may, for example, be a carboxylic acid such as octyic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, olefinic acid, linoleic acid, linolenic acid, ricinoleic acid or behenic acid, or sulfonic acid or sulfinic acid, and the phenol compound may, for example, be 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenylacrylate, 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate or octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate.

The number of deactivation at the polymerizable active terminals is in proportion to the stoichiometric amount of the polymerization terminator added, and accordingly the polymerization terminator may be added in a stoichiometric amount smaller than the number of active terminals divided in several times, so that only a part of active terminals during the polymerization are deactivated, and while polymerization is further continued by the remaining active terminals, and the remaining active terminals is deactivated when a predetermined rate of polymerization is achieved, or the entire active terminals may be deactivated all at once. However, it is necessary to deactivate all the active terminals by adding an adequate amount of the polymerization terminator relative to the number of active terminals at that point at the completion of the polymerization.

As a method to separate the copolymer solution after completion of the deactivation treatment from the solvent, (1) a method of precipitating it in a poor solvent such as methanol, (2) a method of supplying the copolymer solution to e.g. a heated roll, and evaporating the solvent alone to separate the copolymer (drum drier method), (3) a method of supplying the heated block copolymer (composition) solution to a can maintained to a pressure lower than the equilibrium vapor pressure at the temperature of the organic solvent contained in the heated solution continuously or intermittently for devolatilization (flush evaporation method), (4) a method of passing the copolymer solution through a vent type extruder for devolatilization, (5) a method of injecting the copolymer solution into warm water with stirring to evaporate the solvent (steam stripping method), or a combination thereof may be mentioned.

In the present invention, of the block copolymer (A) and/or the copolymer composition containing the block copolymer (A) as an essential component, in the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, there is at least one maximum value within a temperature range of from 60 to 110° C., preferably from 62 to 105° C., particularly preferably from 65 to 100° C., the highest maximum value within this range is preferably from 0.5 to 4.0, particularly preferably from 0.7 to 3.5, the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40%, preferably at most 35% of the highest maximum value, the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10%, preferably at most 8% of the highest maximum value, and

further, the loss tangent value at 30° C. is preferably from 0.01 to 0.4, particularly preferably from 0.01 to 0.2. In other words, the present inventors have found that a heat shrinkable (multilayer) film having favorable spontaneous shrinkage resistance can be obtained without impairing the low temperature shrinkability, by using the block copolymer (A) and/or the copolymer composition containing the block copolymer (A) as an essential component, having a steep maximum value having a high peak shape of the loss tangent value within a temperature range of from 60 to 110° C.

In the present invention, of the block copolymer (A) and/or the copolymer composition containing the block copolymer (A) as an essential component, in the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, if there is no maximum value within a temperature range of from 60 to 110° C., and the temperature for the maximum value exceeds 110° C., the low temperature shrinkability of the obtained heat shrinkable (multilayer) film tends to be inadequate, and if there is no maximum value within a temperature range of from 60 to 110° C., and the temperature for the maximum value is less than 60° C., the spontaneous shrinkage resistance may be inadequate in some cases. Further, if the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value exceeds 40% of the highest maximum value, the value of loss tangent at a temperature lower by 30° C. than the lowest temperature exceeds 10% of the highest maximum value, or the loss tangent value at 30° C. exceeds 0.4, the spontaneous shrinkage resistance tends to be impaired.

Now, the method for producing the block copolymer (A), the loss tangent value of which satisfies the conditions (1) to (3) as defined in claim 1 will be explained in further detail below.

In order that the temperature for the maximum value of the loss tangent value is from 60 to 110° C., it is desirable that a copolymer segment portion having a weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene of from 98/2 to 72/28, preferably from 97/3 to 75/25, particularly preferably from 95/5 to 80/20, is contained in the block copolymer. Needless to say, the temperature for the maximum value of the loss tangent value may be set to a high temperature of from 70 to 110° C. when  $\alpha$ -methylstyrene instead of styrene as the vinyl aromatic hydrocarbon or isoprene instead of butadiene as the conjugated diene is used with a high proportion, or the proportion of vinyl bonds in a microstructure of butadiene is increased. However, if the vinyl bonds increase, if it stays at the time of processing, gel tends to form, and in view of material cost, styrene and butadiene are most preferred as the vinyl aromatic hydrocarbon and as the conjugated diene, respectively, and the proportion of the vinyl bonds is preferably at most 20%, particularly preferably at most 16%, in the microstructure of butadiene, and in such a case, the temperature for the maximum value of the loss tangent value is likely to be controlled to a low temperature of from 60 to 110° C.

If the weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene in the segment portion of the copolymer chain of the vinyl aromatic hydrocarbon and the conjugated diene corresponding to a temperature for the maximum value of the loss tangent value of from 60 to 110° C. exceeds 98/2, the low temperature shrinkability of the obtained heat shrinkable film tends to decrease, on the other hand, if it is less than 72/28, the maximum value of the loss tangent value tends to be less than 60° C., and the spontaneous shrinkage resistance tends to decrease.

In order to obtain a steep peak which satisfies the conditions (2) and (3) among the above conditions for the loss

tangent value, it is preferred that the segment portion of the copolymer chain of the vinyl aromatic hydrocarbon and the conjugated diene corresponding to the maximum value of the loss tangent value within a temperature range of from 60 to 110° C., is polymerized under such conditions that the proportion of the random chain of the vinyl aromatic hydrocarbon and the conjugated diene is high. For example, a method of adding them in small amounts so that the reactive terminals in each monomer polymerization are always in a substantially starved state, or a method of copolymerizing them in the presence of a randomizing agent may be mentioned.

Further, the peak shape of the maximum value of the loss tangent value tends to be broad or the temperature for the maximum value tends to slightly change, under influence of the segment portion adjacent to the segment portion of the copolymer chain of the vinyl aromatic hydrocarbon and the conjugated diene corresponding to a temperature for the maximum value of the loss tangent value of from 60 to 110° C. Thus, preferred is a block copolymer comprising from 0.1 to 50 parts by weight, preferably from 0.2 to 30 parts by weight, particularly preferably from 1 to 15 parts by weight, of the adjacent segment portion comprising a vinyl aromatic hydrocarbon and/or a conjugated diene based on 100 parts by weight of the segment portion of the copolymer chain of the vinyl aromatic hydrocarbon and the conjugated diene corresponding to a temperature for the maximum value of the loss tangent value of from 60 to 110° C. Further, in view of effect of improving heat stability at the time of processing, the segment portion comprising a vinyl aromatic hydrocarbon alone is present on one terminal, particularly on both terminals. For example, in a case of a block copolymer having a segment comprising a vinyl aromatic hydrocarbon alone on one terminal, particularly on both terminals, even if e.g. the edge or the like obtained at the time of extruding or orienting the heat shrinkable (multilayer) film is mixed as a returned material, a sheet or film having favorable orienting processability, low temperature shrinkability, spontaneous shrinkage resistance and transparency can be obtained.

The block copolymer (A) of the present invention may be produced, for example, by the following method taking the above into consideration. However, its production is not limited to the following method.

A method for producing a block copolymer, which comprises polymerizing from 0 to 50 parts by weight of a vinyl aromatic hydrocarbon and/or a conjugated diene as a monomer employing an organic lithium compound as an initiator in an organic solvent (first step), adding 100 parts by weight in total of a vinyl aromatic hydrocarbon and a conjugated diene in a weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene of from 98/2 to 72/28, as mixed or separately, simultaneously, and intermittently or continuously to the reaction system so that the feed rate of the monomers is substantially lower than the reaction rate (second step), and polymerizing from 0.1 to 50 parts by weight of a vinyl aromatic hydrocarbon and/or a conjugated diene as a monomer (third step).

Further, a method for producing a block copolymer may be mentioned, which comprises polymerizing from 0 to 50 parts by weight of a vinyl aromatic hydrocarbon and/or a conjugated diene as a monomer employing an organic lithium compound as an initiator in an organic solvent (first step), adding 100 parts by weight in total of a vinyl aromatic hydrocarbon and a conjugated diene with a weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene of from 98/2 to 72/28 as mixed or separately to the reaction

system in the presence of a randomizing agent for polymerization (second step), and polymerizing from 0.1 to 50 parts by weight of a vinyl aromatic hydrocarbon and/or a conjugated diene as a monomer (third step).

The first step is not necessarily required, but the method is characterized by the polymerization steps of the second and third steps. Each of the first and third steps is not necessarily a single step, and it may be a step of obtaining a block copolymer having at least two segments. For example, the segment portion obtained in the first step may comprise a vinyl aromatic hydrocarbon chain alone, but in the third step, a segment portion of a vinyl aromatic hydrocarbon chain and a segment portion of a conjugated diene chain may be obtained.

The block copolymer (A) as an essential component in the present invention is not particularly limited so long as conditions for the measured values obtained by dynamic viscoelasticity measurement as defined in claims are satisfied. Further, it may be a blended product of the block copolymer (A) with another block copolymer. For example, so long as the main component of the block copolymer (A) is a block copolymer having the above-described random structure segment, the vinyl aromatic hydrocarbon and the conjugated diene may be bonded with a low rate of change of concentration gradient (graded structure) in the other block copolymer, and there is not necessarily a maximum value of the loss tangent value within a range of from 60 to 110° C. For example, in a case where a heat shrinkable (multilayer) film having favorable impact resistance is required, another block copolymer which shows a temperature for the maximum value of the loss tangent value of at most 0° C., not from 60 to 110° C., may be used together.

Further, with the block copolymer (A) of the present invention thus produced, a vinyl aromatic hydrocarbon polymer containing at least one member selected from the following polymers (B1) to (B3) may be mixed as the case requires. In such a case also, the loss tangent value preferably satisfies the conditions (1) to (3) as identified in claim 1 from the viewpoint of the low temperature shrinkability and spontaneous shrinkage resistance:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A)),

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

Now, the polymers (B1) to (B3) will be explained below.

The vinyl aromatic hydrocarbon polymer (B1) may be polyethylene, a vinyl aromatic hydrocarbon/(meth)acrylate and/or (meth)acrylic acid copolymer, or a high-impact polystyrene. For example, polystyrene may be used together in order to increase the rigidity of the obtained film, a high-impact polystyrene may be used together with a purpose of improving blocking properties, and a vinyl aromatic hydrocarbon/(meth)acrylate and/or (meth)acrylic acid copolymer may be used together to improve processability and low temperature orienting properties.

The vinyl aromatic hydrocarbon used for the vinyl aromatic hydrocarbon polymer (B1) in the present invention



may be the vinyl aromatic hydrocarbon as exemplified for the block copolymer (A). Further, the (meth)acrylate monomer may, for example, be methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-methylhexyl acrylate, 2-ethylhexyl acrylate or octyl acrylate, and the (meth)acrylic acid monomer may be acrylic acid or methacrylic acid. Preferred is methyl methacrylate or n-butyl acrylate. Needless to say, at least two types of (meth)acrylate monomer and/or (meth)acrylic acid monomer such as at least two types of methyl methacrylate and n-butyl acrylate, may be used together.

As the vinyl aromatic hydrocarbon and the conjugated diene to be used for the block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (B2), the monomers to be used for production of the block copolymer (A) may be used and are not particularly limited.

Regarding (B3), the monomer to be used for the copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., may be one as exemplified for the vinyl aromatic hydrocarbon polymer (B1), and the refractive index may be adjusted by the type of the monomer and composition. If the refractive index of the copolymer comprising a vinyl aromatic hydrocarbon and a (meth)acrylate is less than 1.550, decrease in transparency tends to be significant when blended with the block copolymer (A) or polystyrene, and if it exceeds 1.580, decrease in transparency tends to be significant when blended with the rubber-like elastic body. Further, as the rubber-like elastic body (b), the block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, a MBS resin or a MBAS resin may be mentioned. Such a rubber-like elastic body may be used alone or as mixed, and the refractive index of the rubber-like elastic body is preferably within a range of from 1.535 to 1.550 so as to keep transparency. By controlling the refractive indices of the copolymer (a) and the rubber-like elastic body (b) within the above ranges, respectively, it is effective to keep transparency when e.g. the edge of a multilayer sheet, a multilayer film or a heat shrinkable multilayer film obtained at the time of extruding/orienting is mixed as a returned material in an amount of at most 50 parts by weight based on 100 parts by weight of the block copolymer (A) or the copolymer composition and/or the vinyl aromatic hydrocarbon polymer (B1) to (B3).

The weight ratio of the copolymer (a) to the rubber-like elastic body (b) is (a)/(b)=60/40 to 97/3, preferably 70/30 to 95/5, more preferably 75/25 to 91/9. If the weight ratio of (a)/(b) is less than 60/40, rigidity tends to be poor, and if it exceeds 97/3, the impact strength tends to be inadequate.

As a method for producing the rubber-modified transparent resin (B3), a method of blending the copolymer (a) with at least one rubber-like elastic body (b) selected from a MBS resin and a MBAS resin obtained by e.g. emulsion polymerization, and a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene obtained by e.g. anionic polymerization, or a method of polymerizing a monomer mixture corresponding to the copolymer (a) by e.g. emulsion polymerization, bulk-suspension polymerization or bulk polymerization in the presence of a random copolymer comprising polybutadiene, a vinyl aromatic hydrocarbon and a conjugated diene or a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, may be mentioned.

In the present invention, the amount of the vinyl aromatic hydrocarbon polymer (B1) to (B3) is preferably at most 100 parts by weight based on 100 parts by weight of the block copolymer (A) and/or its copolymer composition. If it

exceeds 100 parts by weight, it tends to be difficult to satisfy both spontaneous shrinkage resistance and low temperature shrinkability of the obtained heat shrinkable (multilayer) film, or a impact resistance tends to be impaired.

Further, in a case where the vinyl aromatic hydrocarbon polymer (B1) is an opaque high-impact polystyrene, its amount is at most 20 parts by weight, preferably at most 10 parts by weight, particularly preferably at most 5 parts by weight. If it exceeds 20 parts by weight, transparency tends to decrease.

For mixing, melt kneading by means of e.g. an extruder is preferred. Further, formation into a sheet or a film by melt kneading by means of e.g. a sheet extruder or a film extruder is also one of preferred examples.

Into the block copolymer (A) and/or its copolymer composition obtained in the present invention, various additives may further be incorporated as the case requires.

In a case where the block copolymer composition is subjected to various heat treatments, in order to handle deterioration of physical properties when its molded product or the like is used in an oxidizing atmosphere or under irradiation with e.g. ultraviolet rays, or in order to further impart physical properties suitable for the purpose of use, an additive such as a stabilizer, a lubricant, a processing aid, an anti-blocking agent, an antistatic agent, an anti-fogging agent, a weather resistance-improving agent, a softening agent, a plasticizer or a pigment may, for example, be added.

The stabilizer may, for example, be 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenylacrylate or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate, a phenol type antioxidant such as octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate or 2,6-di-tert-butyl-4-methylphenol, or a phosphorus type antioxidant such as 2,2-methylenebis(4,6-di-tert-butylphenyl)octylphosphite, trisnonylphenylphosphite or bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol-di-phosphite.

Further, the lubricant, processing aid, anti-blocking agent, antistatic agent or anti-fogging agent may, for example, be a saturated fatty acid such as palmitic acid, stearic acid or behenic acid, a fatty acid ester or a pentaerythritol fatty acid ester such as octyl palmitate or octyl stearate, a fatty acid amide such as erucamide, oleamide or stearamide, ethylenebis stearamide, a glycerol-mono-fatty acid ester, a glycerol-di-fatty acid ester, or a sorbitan fatty acid ester such as sorbitan-mono-palmitate or sorbitan-mono-stearate, or a higher alcohol represented by myristyl alcohol, cetyl alcohol or stearyl alcohol.

The weather resistance-improving agent may, for example, be a benzotriazole type such as 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, a salicylate type such as 2,4-di-tert-butylphenyl-3',5'-di-tert-butyl-4'-hydroxybenzoate, a benzophenone type ultraviolet absorber such as 2-hydroxy-4-n-octoxybenzophenone, or a hindered amine type weather resistance-improving agent such as tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate. Further, white oil or silicone oil may, for example, be added.

Such an additive is used preferably in an amount of at most 5 parts by weight based on 100 parts by weight of the block copolymer composition.

The block copolymer or the copolymer composition of the present invention is processed into various molded products by a known method such as injection molding, extrusion, compression molding or vacuum molding and used practically. It is preferably used in the form of a sheet or a film, and it is more preferably used as a heat shrinkable film or a heat shrinkable multilayer film.



The single-layer sheet and/or the single-layer film of the present invention are made of the block copolymer (A) and/or its copolymer composition which satisfies the conditions of the loss tangent value, and the single-layer heat shrinkable film can be obtained by orienting the single-layer sheet and/or the single-layer film, by tubular orienting or the like.

As examples of the multilayer film, the multilayer sheet and the heat shrinkable multilayer film of the present invention, a multilayer film, a multilayer sheet and a heat shrinkable multilayer film, having a surface layer (surface and/or rear layer) formed by a copolymer component composed mainly of the block copolymer (A) of the present invention or a copolymer composition containing (A) as an essential component and a layer other than the surface layer (intermediate layer or primary coat) formed by the component (B1) to (B3) and/or a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, and on the contrary, a multilayer film, a multilayer sheet and a heat shrinkable multilayer film having a surface layer formed by the component (B1) to (B3) and/or a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, and a layer other than the surface layer formed by a copolymer component composed mainly of the block copolymer (A) of the present invention or a copolymer composition containing (A) as an essential component, may be mentioned.

As the method for producing the heat shrinkable film and the heat shrinkable multilayer film, a known method may be employed. For example, the heat shrinkable film may be obtained by melting a resin in an extruder, extruding it by means of a die such as a T-die or a ring die to form it into a film, and orienting the film uniaxially, biaxially or multi-axially. Further, the heat shrinkable multilayer film may be obtained by laminating separately melted resins in a die, by means of a feed block or the like and then extruding the layer into a film, and orienting the film uniaxially, biaxially or multi-axially.

In the present invention, the orienting temperature is preferably from 60 to 120° C. If it is less than 60° C., the sheet or the film is likely to break at the time of orienting, and if it exceeds 120° C., no favorable shrinkability will be obtained. The orienting ratio is not particularly limited, but is preferably from 1.5 to 8 times. If it is 1.5 times, the heat shrinkability tends to be inadequate, and if it exceeds 8 times, orienting tends to be difficult. When such a film is used as a heat shrinkable label or a packaging material, the heat shrinkage factor is at least 15% at 80° C., preferably at least 15% at 70° C., particularly preferably at least 20% at 70° C., in view of rapid shrinkage at a low temperature. The thickness of the film is preferably from 10 to 300  $\mu$ m, more preferably from 20 to 100  $\mu$ m.

The copolymer mixture forming the multilayer film or the multilayer sheet of the present invention may, for example, be the multilayer film, the multilayer sheet or the heat shrinkable multilayer film, or the edge generated when such a film is subjected to e.g. extrusion or orienting, or a pulverized product or a re-pelletized product (returned material) thereof. The amount of the copolymer mixture forming the multilayer film or the multilayer sheet is preferably at most 50 parts by weight based on 100 parts by weight of the block copolymer (A) which satisfies the conditions of the loss tangent value or its copolymer composition and/or the vinyl aromatic hydrocarbon copolymer (B1) to (B3). If it exceeds 50 parts by weight, decrease in transparency, impact resistance or the like of the obtained heat shrinkable multilayer film tends to be significant.

Further, in the present invention, an antistatic agent or a lubricant may be coated on the surface so as to improve the surface properties of the obtained film.

As the application of the heat shrinkable film or the thermoplastic multilayer film of the present invention, a heat shrinkable label, a heat shrinkable cap seal, a protective film for bottles, a pack guard shrink packaging, or an electrical insulating coating for e.g. capacitors and dry batteries are particularly preferred, and further, it may be optionally used for a packaging film, a cap material and the like.

Now, the present invention will be explained in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to the following Examples.

Methods for producing a block copolymer (composition) and the like used in Examples will be described below as Reference Examples.

#### REFERENCE EXAMPLE 1

(1) 490 kg of cyclohexane as a polymerization solvent was charged into a reactor and maintained at 80° C. In the following Examples and Comparative Examples, cyclohexane was employed as the polymerization solvent.

(2) 1,300 mL of a 10 wt % cyclohexane solution of n-butyllithium as a polymerization catalyst solution was preliminarily added thereto, and 10.5 kg of a styrene monomer was charged thereto all at once, which was subjected to anionic polymerization. In the following Examples and Comparative Examples, a 10 wt % cyclohexane solution of n-butyllithium was employed as the polymerization catalyst solution.

(3) After the rate of polymerization of the styrene monomer exceeded 99%, while heating the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 170.1 kg and butadiene in a total amount of 18.9 kg were simultaneously added at constant addition rates of 76.5 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(4) 10.5 kg of a styrene monomer was further added all at once to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight (as calculated as polystyrene by GPC, the same applies hereinafter) of 186,000 and having a polystyrene block portion and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 2

(1) Into a reactor, 490 kg of the polymerization solvent and 7.4 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,100 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 50° C., 6.3 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 173.7 kg and butadiene in a total amount of 15.1 kg were simultaneously added thereto at constant addition rates of 97.7 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

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(5) Further, 7.4 kg of a styrene monomer was added all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a molecular weight of 214,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 3

(1) Into a reactor, 490 kg of the polymerization solvent and 84.0 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,700 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the rate of polymerization of the styrene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 50° C., 42 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the rate of polymerization of the butadiene monomer exceeded 99%, after the gas was completely consumed, while maintaining the internal temperature of the reaction system at 50° C., 84.0 kg of a styrene monomer was added to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 149,000 and having a polystyrene block portion and a block portion of polybutadiene.

#### REFERENCE EXAMPLE 4

(1) Into a reactor, 357 kg of the polymerization solvent was charged and maintained at 80° C.

(2) 800 mL of the polymerization catalyst solution was preliminarily added thereto, and 5.4 kg of a styrene monomer was charged thereinto all at once and subjected to anionic polymerization.

(3) After the rate of polymerization of the styrene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 130.9 kg and butadiene in a total amount of 11.4 kg were simultaneously added thereto at constant addition rates of 97.6 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(4) Further, 5.4 kg of a styrene monomer was added thereto all at once to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 205,000 and having a polystyrene block portion and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 5

(1) Into a reactor, 490 kg of the polymerization solvent and 6.3 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,620 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 50° C., 31.5 kg of butadiene was added thereto all at once, and it was successively reacted.

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(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 152.7 kg and butadiene in a total amount of 13.2 kg were simultaneously added thereto at constant addition rates of 98.3 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(5) Further, 6.3 kg of a styrene monomer was added all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a molecular weight of 146,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 6

(1) Into a reactor, 490 kg of the polymerization solvent and 6.3 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,600 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 2.6 kg and butadiene in a total amount of 22.7 kg were simultaneously added at constant addition rates of 8.0 kg/h and 72 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(4) After the styrene monomer and the butadiene gas were completely consumed, while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 158.4 kg and butadiene in a total amount of 13.7 kg were simultaneously added thereto at constant addition rates of 98.3 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(5) Further, 6.3 kg of a styrene monomer was added all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a molecular weight of 152,000 and having a polystyrene block portion and two types of structure portions having different concentration proportion of styrene and butadiene.

#### REFERENCE EXAMPLE 7

(1) Into a reactor, 490 kg of the polymerization solvent and 5.3 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,620 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 50° C., 21.0 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 155.4 kg and butadiene in a total amount of 23.1 kg were simultaneously added thereto at constant addition rates of 57.6 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(5) After the internal temperature was lowered to 50° C., 5.3 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(6) Then, all the polymerizable active terminals were deactivated with water to obtain a polymer having a molecular weight of 155,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene, as a polymer liquid A.

(7) The same operation as for preparation of the polymer liquid A was carried out except that the amount of the polymerization catalyst solution was 1,240 mL to obtain a polymer liquid B having the same molecular structure and having a molecular weight of 218,000.

(8) 200 Parts by weight of the polymer liquid B was mixed with 100 parts by weight of the above-described polymer liquid A, followed by devolatilization to obtain an intended polymer.

#### REFERENCE EXAMPLE 8

(1) Into a reactor, 525 kg of the polymerization solvent and 56.5 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,700 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 30° C., 16.9 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 78.3 kg and butadiene in a total amount of 16.9 kg were simultaneously added thereto at constant addition rates of 77.1 kg/h and 16.6 kg/h, respectively, and the state was kept as it was for 10 minutes after completion of the addition.

(5) After the internal temperature was lowered to 50° C., 56.5 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a molecular weight of 178,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 9

(1) Into a reactor, 385 kg of the polymerization solvent and 57.8 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,700 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 45° C., 49.5 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 60° C., 57.8 kg of a styrene monomer was added thereto to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a molecular weight of 118,000 and having a polystyrene block portion and a block portion of polybutadiene.

#### REFERENCE EXAMPLE 10

(1) Into a reactor, 490 kg of the polymerization solvent, 16.0 kg of  $\alpha$ -methylstyrene and 68.0 kg of a styrene monomer were charged and maintained at 40° C.

(2) 1,500 mL of the polymerization catalyst solution was added thereto, and the vinyl aromatics monomers were subjected to anionic polymerization.

(3) After the vinyl aromatic monomers were completely consumed, while maintaining the internal temperature of the reaction system at 50° C., 4.2 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 50° C., 16.0 kg of  $\alpha$ -methylstyrene and 68.0 kg of a styrene monomer were added thereto and polymerized.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a molecular weight of 143,000 and having a polyvinyl aromatic block portion and a block portion of polybutadiene.

#### REFERENCE EXAMPLE 11

(1) Into a reactor, 245 kg of the polymerization solvent and 3.6 kg of a styrene monomer were charged and maintained at 30° C.

(2) 600 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 40° C., 8.3 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After butadiene and the styrene monomer were completely consumed, while maintaining the internal temperature of the reaction system at 80° C., successively a styrene monomer in a total amount of 50.1 kg and butadiene in a total amount of 20.6 kg were simultaneously added thereto at constant addition rates of 57.7 kg/h and 23.7 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(5) After the internal temperature was lowered to 50° C., 3.6 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having weight average a molecular weight of 182,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 12

(1) Into a reactor, 490 kg of the polymerization solvent and 7.4 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,100 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the rate of polymerization of the styrene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 50° C., 6.3 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the rate of polymerization of the butadiene monomer exceeded 99%, while maintaining the internal

temperature of the reaction system at 80° C., a styrene monomer in a total amount of 160.5 kg and butadiene in a total amount of 28.3 kg were simultaneously added thereto at constant addition rates of 53.5 kg/h and 9.4 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(5) Further, 7.4 kg of a styrene monomer was added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 214,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 13

(1) Into a reactor, 490 kg of the polymerization solvent and 6.3 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,620 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the rate of polymerization of the styrene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 189.2 kg and butadiene in a total amount of 8.2 kg were simultaneously added thereto at constant addition rates of 52.0 kg/h and 2.3 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(4) Further, 6.3 kg of a styrene monomer was added thereto all at once to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 145,000 and having a polystyrene block portion and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 14

(1) Into a reactor, 525 kg of the polymerization solvent and 45.0 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,700 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the rate of polymerization of the styrene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 30° C., 9.0 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the rate of polymerization of the butadiene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 121.2 kg and butadiene in a total amount of 16.1 kg were simultaneously added thereto at constant addition rates of 181.9 kg/h and 24.2 kg/h, respectively, and the state was kept as it was for 20 minutes after completion of the addition.

(5) After the internal temperature was lowered to 50° C., 33.8 kg of the styrene monomer was further added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 175,000 and having a polystyrene block portion, a block

portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 15

(1) Into a reactor, 525 kg of the polymerization solvent and 56.5 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,700 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the rate of polymerization of the styrene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 30° C., 19.9 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the rate of polymerization of the butadiene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 80° C., successively a styrene monomer in a total amount of 78.3 kg and butadiene in a total amount of 13.9 kg were simultaneously added thereto at constant addition rates of 117.5 kg/h and 20.9 kg/h, respectively, and the state was kept as it was for 10 minutes after completion of the addition.

(5) After the internal temperature was lowered to 50° C., 56.5 kg of a styrene monomer was added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 178,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 16

(1) Into a reactor, 525 kg of the polymerization solvent and 7.9 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,700 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the rate of polymerization of the styrene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 30° C., successively a styrene monomer in a total amount of 184.2 kg and butadiene in a total amount of 25.1 kg were simultaneously added thereto all at once, and polymerized while water cooling was strengthened so that the temperature of the reaction system would not exceed 70° C.

(4) After the rates of polymerization of butadiene and the styrene monomer exceeded 99% respectively, the internal temperature was lowered to 50° C., and then 7.9 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 176,000 and having a polystyrene block portion and a graded structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 17

(1) Into a reactor, 490 kg of the polymerization solvent and 8.4 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,200 mL of a 10 wt % cyclohexane solution of n-butyllithium (hereinafter referred to as polymerization

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catalyst solution) was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) Polymerization was carried out until the rate of polymerization of the styrene monomer exceeded 99%, and then while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 92.4 kg and butadiene in a total amount of 11.3 kg were simultaneously added thereto at constant addition rates of 61.3 kg/h and 7.5 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(4) Polymerization was carried out until the rate of polymerization of butadiene exceeded 99%, and then while maintaining the internal temperature of the reaction system at 80° C., 24.4 kg of butadiene was added thereto all at once, and it was successively reacted.

(5) 73.5 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a polybutylene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 18

(1) Into a reactor, 490 kg of the polymerization solvent and 8.4 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,830 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) Polymerization was carried out until the rate of polymerization of the styrene monomer exceeded 99%, and then while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 113.4 kg and butadiene in a total amount of 10.1 kg were simultaneously added thereto at constant addition rates of 75.2 kg/h and 6.7 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(4) Polymerization was carried out until the rate of polymerization of butadiene exceeded 99%, and then while maintaining the internal temperature of the reaction system at 80° C., 25.6 kg of butadiene was added thereto all at once, and it was successively reacted.

(5) 52.5 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a polybutylene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 19

(1) Into a reactor, 490 kg of cyclohexane as the polymerization solvent was charged and maintained at 80° C.

(2) 820 mL of the polymerization catalyst solution, 35 g of potassium tert-butoxide as a randomizing agent and 70 g of tetrahydrofuran were preliminarily added thereto, and 9.5 kg of a styrene monomer was charged thereto all at once, and anionic polymerization was carried out until the rate of polymerization of the styrene monomer exceeded 99%.

(3) While maintaining the internal temperature of the reaction system at 80° C., 37.8 kg of a styrene monomer and

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1.7 kg of butadiene were simultaneously charged thereto, and maintained until the rates of polymerization of the styrene monomer and butadiene exceeded 99%. This operation was repeated five times in total.

(4) Further, 3.2 kg of a styrene monomer was added thereto all at once to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a polystyrene block portion and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 20

(1) Into a reactor, 368 kg of the polymerization solvent and 6.3 kg of a styrene monomer were charged and maintained at 30° C.

(2) 910 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) Polymerization was carried out until the rate of polymerization of the styrene monomer exceeded 99%, and then while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 101.1 kg and butadiene in a total amount of 14.2 kg were simultaneously added thereto at constant addition rates of 67.1 g/h and 9.5 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(4) Polymerization was carried out until the rate of polymerization of butadiene exceeded 99%, and then while maintaining the internal temperature of the reaction system at 80° C., 12.6 kg of butadiene was added thereto all at once, and it was successively reacted.

(5) Further, 23.7 kg of a styrene monomer was added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 21

(1) Into a reactor, 490 kg of the polymerization solvent and 8.4 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,650 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) Polymerization was carried out until the rate of polymerization of the styrene monomer exceeded 99%, and then while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 92.4 kg and butadiene in a total amount of 11.3 kg were simultaneously added thereto at constant addition rates of 61.3 kg/h and 7.5 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(4) Polymerization was carried out until the rate of polymerization of butadiene exceeded 99%, and then while maintaining the internal temperature of the reaction system at 80° C., 24.4 kg of butadiene was added thereto all at once, and it was successively reacted.

(5) Further, 73.5 kg of a styrene monomer was added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing

a polymer having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 22

(1) Into a reactor, 490 kg of the polymerization solvent and 6.3 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,620 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the rate of polymerization of the styrene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 50° C., 34.6 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the rate of polymerization of the butadiene monomer exceeded 99%, while maintaining the internal temperature of the reaction system at 80° C., a styrene monomer in a total amount of 156.0 kg and butadiene in a total amount of 6.8 kg were simultaneously added thereto at constant addition rates of 52.0 kg/h and 2.3 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(5) Further, 6.3 kg of a styrene monomer was added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 146,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 23

(1) Into a reactor, 490 kg of cyclohexane as the polymerization solvent was charged and maintained at 80° C.

(2) 1,650 mL of a 10 wt % cyclohexane solution of n-butyllithium as the polymerization catalyst solution, 35 g of potassium tert-butoxide as a randomizing agent and 70 g of tetrahydrofuran were preliminarily added thereto, and 10.5 kg of a styrene monomer was charged thereto all at once and subjected to anionic polymerization until the rate of polymerization of the styrene monomer exceeded 99%.

(3) Then, while maintaining the internal temperature of the reaction system at 80° C., 34 kg of a styrene monomer and 3.8 kg of butadiene were simultaneously charged thereto, and maintained until the rates of polymerization of the styrene monomer and butadiene exceeded 99% respectively. This operation was repeated five times in total.

(4) Further, 10.5 kg of a styrene monomer was added thereto all at once to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 159,000 and having a polystyrene block portion and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 24

(1) Into a reactor, 525 kg of the polymerization solvent and 8.4 kg of a styrene monomer were charged and maintained at 30° C. In the following Examples and Comparative Examples, cyclohexane was employed as the polymerization solvent.

(2) 1,240 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to

anionic polymerization. In the following Examples and Comparative Examples, a 10 wt % cyclohexane solution of n-butyllithium was employed as the polymerization catalyst solution.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 30° C., 14.7 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 80° C., successively a styrene monomer in a total amount of 155.3 kg and butadiene in a total amount of 23.2 kg were simultaneously added thereto at constant addition rates of 56.9 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 10 minutes after completion of the addition.

(5) After the internal temperature was lowered to 50° C., 8.4 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight (value as calculated as polystyrene by GPC, the same applies hereinafter) of 204,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 25

(1) Into a reactor, 490 kg of the polymerization solvent and 8.4 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,990 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 50° C., 22.1 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 80° C., successively a styrene monomer in a total amount of 157.5 kg and butadiene in a total amount of 13.7 kg were simultaneously added thereto at constant addition rates of 97.7 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 5 minutes after completion of the addition.

(5) After the internal temperature was lowered to 50° C., 8.4 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 127,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

#### REFERENCE EXAMPLE 26

(1) Into a reactor, 525 kg of the polymerization solvent and 8.4 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,680 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction

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system at 30° C., 8.5 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 80° C., successively a styrene monomer in a total amount of 162.0 kg and butadiene in a total amount of 22.7 kg were simultaneously added thereto at constant addition rates of 60.7 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 10 minutes after completion of the addition.

(5) After the internal temperature was lowered to 50° C., 8.4 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 151,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

## REFERENCE EXAMPLE 27

(1) Into a reactor, 525 kg of the polymerization solvent and 71.7 kg of a styrene monomer were charged and maintained at 30° C.

(2) 2,120 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 30° C., 25.3 kg of butadiene was added thereto all at once and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 30° C., 107.5 kg of a styrene monomer and 6.3 kg of butadiene were further added thereto all at once to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 119,000 and having a polystyrene block portion, a block portion of polybutadiene and a graded structure portion of styrene and butadiene.

## REFERENCE EXAMPLE 28

(1) Into a reactor, 525 kg of the polymerization solvent and 8.4 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,830 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 30° C., 8.5 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 80° C., successively a styrene monomer in a total amount of 162.0 kg and butadiene in a total amount of 22.7 kg were simultaneously added thereto at constant addition rates of 60.7 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 10 minutes after completion of the addition.

(5) After the internal temperature was lowered to 50° C., 8.4 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

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(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 139,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

## REFERENCE EXAMPLE 29

(1) Into a reactor, 525 kg of the polymerization solvent and 71.7 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,420 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 30° C., 31.6 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature at 50° C., 107.5 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 182,000 and divided into a polystyrene block portion and a polybutadiene block portion.

## REFERENCE EXAMPLE 30

(1) Into a reactor, 525 kg of the polymerization solvent and 31.5 kg of a styrene monomer were charged and maintained at 30° C.

(2) 1,020 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 30° C., 16.8 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature of the reaction system at 80° C., successively a styrene monomer in a total amount of 134.4 kg and butadiene in a total amount of 18.9 kg were simultaneously added thereto at constant addition rates of 60.4 kg/h and 8.5 kg/h, respectively, and the state was kept as it was for 10 minutes after completion of the addition.

(5) After the internal temperature was lowered to 50° C., 8.4 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(6) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 252,000 and having a polystyrene block portion, a block portion of polybutadiene and a random structure portion of styrene and butadiene.

## REFERENCE EXAMPLE 31

(1) Into a reactor, 525 kg of the polymerization solvent and 86.1 kg of a styrene monomer were charged and maintained at 30° C.

(2) 5,100 mL of the polymerization catalyst solution was added thereto, and the styrene monomer was subjected to anionic polymerization.

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(3) After the styrene monomer was completely consumed, while maintaining the internal temperature of the reaction system at 30° C., 37.8 kg of butadiene was added thereto all at once, and it was successively reacted.

(4) After the butadiene gas was completely consumed, while maintaining the internal temperature at 50° C., 86.1 kg of a styrene monomer was further added thereto all at once to complete the polymerization.

(5) Finally, all the polymerizable active terminals were deactivated with water to obtain a polymer liquid containing a polymer having a weight average molecular weight of 49,000 and divided into a polystyrene block portion and a polybutadiene block portion.

## REFERENCE EXAMPLE 32

(1) Into an autoclave equipped with a stirrer having an internal capacity of 250 L, 120 kg of pure water, 120 g of tribasic calcium phosphate as a dispersion stabilizer, 0.12 g of potassium persulfate and 0.06 g of sodium dodecylbenzenesulfonate were added and stirred at 100 rpm.

(2) Then, a solution having 70 kg of styrene, 15 kg of methyl methacrylate, 15 kg of n-butyl acrylate, 200 g of t-butylperoxy-2-ethylhexanoate and 50 g of 1,1-bis(t-hexylperoxy)3,3,5-trimethylcyclohexane as initiators, and 50 g of  $\alpha$ -methylstyrene dimer as a chain transfer agent mixed therein, was charged thereto, the autoclave was sealed, and polymerization was carried out at 90° C. for 6 hours and at 120° C. for 2 hours.

(3) Beads obtained by the polymerization were neutralized, washed, dehydrated and dried, and then a copolymer resin in the form of pellets was obtained by using an extruder. The weight average molecular weight was 260,000.

## REFERENCE EXAMPLE 33

(1) To an autoclave having a capacity of 200 L, 115 kg of pure water, 500 g of potassium oleate, 75 g of sodium pyrophosphate, 1.5 g of ferrous sulfate, 2.2 g of sodium ethylenediaminetetraacetate and 22 g of Rongalite were added and uniformly dissolved with stirring.

(2) Then, 20.0 kg of styrene, 30.0 kg of butadiene, 148 g of t-dodecylmercaptan, 30 g of divinylbenzene and 96 g of diisopropylbenzene hydroperoxide were added thereto, and reaction was carried out with stirring at 50° C. for 16 hours to complete the polymerization, and a rubber polymer latex was obtained.

(3) To the obtained rubber-like polymer latex, 45 g of sodium sulfosuccinate was added for adequate stabilization, and then a 0.2% hydrochloric acid aqueous solution and a 2% caustic acid aqueous solution were added thereto from separate nozzles while maintaining the pH of the latex at from 8 to 9, by adjusting the addition rates, stirring rate and the like, for agglomeration and enlargement of latex to obtain a rubber-like elastic body latex having an average particle size of 0.35  $\mu$ m.

(4) 30 kg of the rubber-like elastic body latex as calculated as a solid content was weighed and transferred to an autoclave having a capacity of 200 L, 80 kg of pure water was added thereto, and the temperature was raised to 50° C. in a stream of nitrogen while stirring.

(5) 2 kg of pure water having 1.25 g of ferrous sulfate, 2.5 g of sodium ethylenediaminetetraacetate and 100 g of Rongalite dissolved therein was added thereto, and a mixture comprising 16 kg of styrene, 14 kg of methyl methacrylate and 60 g of t-dodecylmercaptan, and a solution having 120

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g of diisopropylbenzene hydroperoxide dispersed in 8 kg of pure water containing 450 g of potassium oleate, were separately added thereto continuously over a period of 6 hours.

(6) After completion of the addition, the temperature was raised to 70° C., 30 g of diisopropylbenzene hydroperoxide was added thereto, and then the mixture was left to stand for 2 hours to complete the polymerization.

(7) An antioxidant was added to the obtained emulsion, the solid content was diluted to 15% with pure water, then the temperature was raised to 60° C., and diluted sulfuric acid was added thereto with vigorously stirring for salting-out, and the temperature was raised to 90° C. for solidification.

(8) Finally, dehydration, washing with water and drying were carried out to obtain a powder type graft copolymer.

The refractive index was 1.548 as calculated from the composition of the monomer units constituting the obtained graft copolymer.

Each of the polymers of Reference Examples, Examples and Comparative Examples in a solution state was, after preliminary concentration of the polymerization solvent by itself or in a mixed state in a predetermined weight ratio, subjected to devolatilization treatment by means of a vent type extruder and formed into pellets, which were subjected to granulation with the composition as it was or after melt-mixed again with a polymer of another Reference Example or the like, and subjected to the following tests.

Further, for some of the compositions and the multilayer films of Examples and Comparative Examples of the present invention, in addition to e.g. the block copolymers of e.g. Reference Examples, a general purpose polystyrene having a weight average molecular weight of 270,000, high-impact polystyrene (manufactured by TOYO-STYRENE CO., LTD.: E640N) or a SBS resin (manufactured by Denki Kagaku Kogyo K.K.: CLEAREN 730L) was employed. The data of the weight average molecular weight and dynamic viscoelasticity regarding CLEAREN 730L is shown in Table 22.

In a case where the block copolymer (composition) of the present invention and these resins were combined to form a composition, a method of melt-kneading pellets to form a pellet-form resin composition again was employed.

Of each of the block copolymers (compositions) of Reference Examples, Examples and Comparative Examples, the molecular weight, the refractive index, the temperature dependency of dynamic viscoelasticity behavior, the heat shrinkage factor, the spontaneous shrinkage factor and Haze (cloudiness) were measured by the following methods depending upon the purpose.

## Measurement of Molecular Weight

The weight average molecular weight was measured by means of the following GPC measuring apparatus under the following conditions.

Apparatus: "SYSTEM-21 Shodex (Showa Denko K.K.)

Column: three columns of PL gel MIXED-B in series

Temperature: 40° C.

Detection: differential refractive index

Solvent: tetrahydrofuran

Concentration: 2 wt %

Analytical curve: prepared by using standard polystyrene (manufactured by PL), and the weight average molecular weight was represented as calculated as polystyrene.

The weight average molecular weight of the aromatic hydrocarbon block incorporated in the block copolymer



obtained as the case requires, is a value obtained by GPC measurement of the vinyl aromatic hydrocarbon polymer component obtained by ozonolysis of the block copolymer [Y. TANAKA, et al., RUBBER CHEMISTRY AND TECHNOLOGY, 58, 16 (1985)] and calculation in accordance with the above method.

#### Measurement of Dynamic Viscoelasticity

The loss tangent value of each of the polymers (compositions) of Reference Examples, Examples and Comparative Examples was measured by means of dynamic viscoelasticity method in accordance with the following procedure.

(1) Pellets of each polymer were pressed under heating at from 200 to 250° C. to prepare a sheet having a thickness of from 0.1 to 0.5 mm.

(2) From this sheet, a test specimen having an appropriate size was cut out, stored in a room at 23° C. at 50% RH for at least 24 hours to carry out curing treatment, and then the storage elastic modulus and loss elastic modulus characteristic to the polymer in the form of the test specimen were measured by using the following apparatus while changing the temperature, and the loss tangent value was calculated.

Apparatus: solid viscoelasticity measuring apparatus RSA2 manufactured by Rheometrics

Temperature range: room temperature to 130° C.

Temperature-raising rate: 4° C./min

Measurement frequency: 1 Hz

#### Measurement of Refractive Index

The refractive index of the polymer produced in Reference Example 32 was measured in accordance with the following procedure.

(1) A test specimen having a size of 120 mm×120 mm×2 mm was formed by means of an injection molding machine (IS-80CVN) manufactured by TOSHIBA MACHINE CO. LTD. at a cylinder temperature of 220° C.

(2) Using the test specimen, the refractive index was measured by using the following apparatus under the following conditions in accordance with JIS K7105.

Apparatus: digital refractometer RX-2000 manufactured by ATAGO CO., LTD.

Temperature: 25° C.

The refractive index of the copolymer resin at 25° C. was 1.561.

As it is difficult to actually measure the refractive index of the graft copolymer of Reference Example 33, in the present specification, the compositional ratio of the monomer units constituting the graft copolymer is measured by means of composition analysis, and the refractive index is obtained by calculation by means of the following formula:

$$N = XA_n nA + XB_n nB + XC_n nC + \dots$$

Namely, in a case where the composition of the monomer units constituting the graft copolymer comprises an Am monomer: XA, a Bm monomer: XB and a Cm monomer: XC (provided that XA+XB+XC=1 by the weight ratio), it is presumed that nA means the refractive index of the polymer consisting of the Am monomer, nB means the refractive index of the polymer consisting of the Bm monomer, and nC means the refractive index of the polymer consisting of the Cm monomer, and the refractive index of the copolymer is obtained by calculation by assigning these values to the above formula. The refractive index as calculated from the composition of the monomer units constituting the obtained graft copolymer was 1.548.

An oriented film for measurement of the heat shrinkability and spontaneous shrinkability of the heat shrinkable film

made of the block copolymer (composition) of the present invention was prepared in accordance with the following procedure.

(1) Pellets in each of Examples and Comparative Examples were formed into an extruded sheet having a thickness of 0.25 mm by means of the following apparatus ①, and a sheet piece of 9 cm square was cut out from the sheet along the extrusion direction axis (the direction along the extrusion axis will be referred to as "MD direction", and the direction perpendicular to the MD direction will be referred to as "TD direction").

(2) The sheet piece was oriented five times in the TD direction while heating at a predetermined temperature as identified in each of Tables 4 to 12 by means of the following apparatus ② to prepare a heat shrinkable film.

Apparatus ①: 40 mmφ single axis extruder VE40 (with a T-die with a width of 40 cm) manufactured by Tanabe Plastic Kikai K.K.

Apparatus ②: biaxial orienting machine manufactured by Toyo Seiki K.K.

A heat shrinkable multilayer film was prepared in such a manner that a multilayer sheet with a predetermined layer constitution with a thickness of 0.25 mm was obtained by means of a multilayer sheet extruder with feed block, and the multilayer sheet was oriented in the same manner as for a single layer oriented film.

#### Measurement of Film Formation Property

The film formation property of each of the resin compositions of Examples and Comparative Examples was judged as follows by visually observing the state (surface roughening, presence or absence of striped patterns) of the surface of the oriented film.

o: favorable film formation property with no surface roughening or striped pattern observed

Δ: slight surface roughening or striped pattern observed

X: inadequate improvement with surface roughening or striped pattern confirmed

#### Measurement of Heat Shrinkage Factor

The heat shrinkage factor of the obtained oriented film was measured by the following method.

(1) A test specimen having a size of 10 mm in the MD direction and 120 mm in the TD direction was cut out from the oriented film.

(2) Marked lines with an interval of 100.0 mm were drawn in the TD direction of the test specimen.

(3) The test specimen was immersed in warm water of 70° C. for 30 seconds and taken out. The attached moisture was wiped out, and the distance L between the marked lines was measured by means of a caliper down to 0.1 mm.

(4) The heat shrinkage factor was calculated by the following formula. A heat shrinkage factor of at least 15% was used as a guide for practical use:

$$\text{Heat shrinkage factor (\%)} = \{(100.0 - L) / 100.0\} \times 100$$

#### Measurement of Spontaneous Shrinkage Factor

The spontaneous shrinkage factor of the oriented film was measured by the following method.

(1) From an oriented film prepared under the same conditions as for the oriented film, the heat shrinkage factor of which was measured, a test specimen having a size of about 75 mm in the MD direction and about 400 mm in the TD direction was cut out.

(2) Marked lines with an interval of 300.0 mm were drawn in the TD direction of the test specimen.

(3) The oriented film was stored in an environmental testing machine of 30° C.

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(4) After storage of 30 days, the film was taken out, and the distance L (mm) between the marked lines was measured by means of a caliper down to 0.1 mm.

(5) The spontaneous shrinkage factor was calculated from the following formula. A spontaneous shrinkage factor not exceeding 1.5% relative to a conventional material was employed as a guideline of improvement:

$$\text{Spontaneous shrinkage factor (\%)} = \{(300.0 - L) / 300.0\} \times 100$$

#### Measurement of Cloudiness

The cloudiness of the oriented film was measured by means of the following apparatus in accordance with ASTM D1003.

Apparatus: Haze meter NDH-1001DP model manufactured by Nippon Denshoku Industries Co., Ltd.

#### EXAMPLES

As Examples 1 to 57 and Comparative Examples 1 to 12, using each of the block copolymers as identified in the above Reference Examples 1 to 31 by itself, as a composition with a product of another Reference Example or as a composition with another resin, or each of the vinyl aromatic hydrocarbon polymers of Reference Examples 32 and 33, formation was carried out by the following method into each of formulations as identified in Tables 1 to 21, and the physical properties were evaluated. The evaluation results are also shown in Tables 1 to 21.

As evident from the results shown in Tables, in Examples regarding the block copolymer (composition) of the present

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invention and a film made of it, the low temperature shrinkability, the spontaneous shrinkage resistance, the range of the orienting conditions and the outer appearance were excellent, whereas in comparison regarding a composition and a film which do not satisfy the conditions of the present invention, any of low temperature shrinkability, spontaneous shrinkage resistance, film formation property and the outer appearance of the film was poor.

In Tables 1 to 4, Examples wherein the heat shrinkage factor and the spontaneous shrinkage factor of a heat shrinkable film and a heat shrinkable multilayer film made of a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene wherein the loss tangent value by dynamic viscoelasticity measurement has at least one maximum value within a temperature range of from 60 to 110° C., the loss tangent value at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and the loss tangent value at a temperature lower by 30° C. than the lowest temperature for the maximum value is at most 10% of the highest maximum value, were measured, are shown, and Comparative Examples are also shown.

By comparison among measured values in Tables 1 to 4, it is found that the block copolymer which satisfies conditions of the dynamic viscoelasticity behaviors, the heat shrinkable film and the heat shrinkable multilayer film made of the composition, satisfy favorable heat shrinkability and spontaneous shrinkage resistance.

TABLE 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Block copolymer	Ref. Ex. 1	Ref. Ex. 2	Ref. Ex. 3	Ref. Ex. 4	Ref. Ex. 5	Ref. Ex. 6	Ref. Ex. 7
Temperature at which loss tangent value reaches maximum value within a range of from 60 to 110° C.: T (° C.)	81	80	105	85	93	92	73
Loss tangent value at temperature T° C.: X	2.80	2.79	2.49	2.18	2.42	3.40	2.43
Loss tangent value at a temperature of (T - 10)° C.: Y	0.61	0.71	0.45	0.35	0.75	0.74	0.70
Loss tangent value at a temperature of (T - 30)° C.: Z	0.04	0.07	0.12	0.08	0.14	0.12	0.06
Loss tangent value at 30° C.	0.02	0.03	0.04	0.03	0.03	0.03	0.03
Y/X × 100 (%)	21.8	25.4	18.1	16.1	31.0	21.8	28.8
Z/X × 100 (%)	1.4	2.5	4.8	3.7	5.8	3.5	2.5
Heat Shrinkage factor							
Orienting temperature (° C.)	93	93	113	93	102	102	85
Heat shrinkage factor (%)	20	18	15	22	15	16	23
Orienting temperature (° C.)	81	81	105	85	93	93	75
Heat shrinkage factor (%)	46	44	36	44	31	41	48
Orienting temperature (° C.)	81	81	105	85	93	93	75
Spontaneous shrinkage factor (%)	0.7	0.6	0.4	0.6	0.6	0.5	1.1

Heat shrinkage factor: Measured value regarding a film immersed in warm water of 80° C. for 30 seconds.

Spontaneous shrinkage factor: Measured value regarding a film stored in an environment at 30° C. for 30 days.

TABLE 2

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Block copolymer	Ref. Ex. 8	Ref. Ex. 9	Ref. Ex. 10	Ref. Ex. 11
Temperature at which loss tangent value reaches maximum value within a range of from 50 to 120° C.: T (° C.)	83	108	114	55

TABLE 2-continued

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Loss tangent value at temperature T° C.: X	1.02	1.93	2.38	1.93
Loss tangent value at a temperature of (T - 10)° C.: Y	0.69	0.99	0.50	0.95
Loss tangent value at a temperature of (T - 30)° C.: Z	0.28	0.18	0.15	0.30
Loss tangent value at 30° C.	0.11	0.04	0.05	0.42
Y/X × 100 (%)	67.6	51.3	21.0	49.2
Z/X × 100 (%)	27.5	9.3	6.3	15.5
<u>Heat Shrinkage factor</u>				
Orienting temperature (° C.)	96	116	122	78
Heat shrinkage factor (%)	20	15	8	27
Orienting temperature (° C.)	81	108	114	67
Heat shrinkage factor (%)	39	28	18	51
Orienting temperature (° C.)	81	108	114	67
Spontaneous shrinkage factor (%)	2.7	1.8	0.2	8.9

Heat shrinkage factor: Measured value regarding a film immersed in warm water of 80° C. for 30 seconds.  
 Spontaneous shrinkage factor: Measured value regarding a film stored in an environment at 30° C. for 30 days.

TABLE 3

	Ex. 8	Ex. 9	Ex. 10	Ex. 11
<u>Blend ratio</u>				
Type	Ex. 1	Ex. 1	Ex. 7	Ex. 7
wt %	90	60	65	65
Type	Comp. Ex. 1	Comp. Ex. 2	GPPS	GPPS
wt %	10	40	35	34.5
Type				E640N
wt %				0.5
Temperature at which loss tangent value reaches maximum value within a range of from 60 to 110° C.: T (° C.)	82	81 106	73 108	74 108
Loss tangent value at temperature T for maximum value: X	2.60	2.14 0.47	1.57 0.72	1.61 0.71
Loss tangent value at a temperature of (Tmax - 10)° C.: Y	0.62	0.53	0.52	0.54
Loss tangent value at a temperature of (Tmax - 30)° C.: Z	0.07	0. 04	0.05	0.06
Loss tangent value at 30° C.	0.04	0. 03	0.03	0.03
Y/X × 100 (%)	23.8	24.8	33.1	33.5
Z/X × 100 (%)	2.7	1.9	3.2	3.7
<u>Heat Shrinkage factor</u>				
Orienting temperature (° C.)	93	93	85	85
Heat shrinkage factor (%)	20	18	15	22
Orienting temperature (° C.)	81	81	75	75
Heat shrinkage factor (%)	44	41	40	42
Orienting temperature (° C.)	81	81	75	75
Spontaneous shrinkage factor (%)	0.8	0.7	0.9	0.9

Heat shrinkage factor: Measured value regarding a film immersed in warm water of 80° C. for 30 seconds.  
 Spontaneous shrinkage factor: Measured value regarding a film stored in an environment at 30° C. for 30 days.  
 Tmax: Temperature for the highest maximum value

TABLE 4

	Ex. 12	Ex. 13	Ex. 14	Comp. Ex. 5
<u>Surface layer and rear layer</u>				
Type	730 L	Ex. 1	730 L	730 L
wt %	99.5	100	70	100

TABLE 4-continued

	Ex. 12	Ex. 13	Ex. 14	Comp. Ex. 5
Type	E640N		Returned material	
wt % Intermediate layer	0.5		30	
Type	Ex. 1	730L	Ex. 1	Comp. Ex. 1
wt %	100	100	70	100
Type			Returned material	
wt %			30	
Thickness ratio of surface/intermediate /rear layers	10/80/10	10/80/10	10/80/10	10/80/10
Heat Shrinkage factor				
Orienting temperature (° C.)	93	93	93	93
Heat shrinkage factor (%)	15	16	23	18
Orienting temperature (° C.)	81	81	81	81
Heat shrinkage factor (%)	45	40	44	43
Orienting temperature (° C.)	81	81	81	81
Spontaneous shrinkage factor (%)	0.9	0.8	0.9	2.6

Heat shrinkage factor: Measured value regarding a film immersed in warm water of 80° C. for 30 seconds.

Spontaneous shrinkage factor: Measured value regarding a film stored in an environment at 30° C. for 30 days.

Returned material: Heat shrinkable multilayer film of Ex. 12 pulverized and then re-extruded.

In Tables 5 to 9, Examples wherein the heat shrinkage factor, the spontaneous shrinkage factor and the cloudiness of a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, wherein the loss tangent value by dynamic viscoelasticity measurement has at least one maximum value within a range of from 60 to 110° C., the loss tangent value at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and the loss tangent value at a temperature lower by 30° C. than the lowest temperature for the maximum value is at most 10% of the

highest maximum value, and a heat shrinkable film and a heat shrinkable multilayer film made of the specific composition, were measured, are shown, and Comparative Examples are also shown.

By comparison among values in Tables 5 to 9, it is found that the block copolymer which satisfies the conditions of the dynamic viscoelasticity behaviors, and the heat shrinkable film and the heat shrinkable multilayer film made of the specific composition, satisfy transparency while they have favorable heat shrinkability and spontaneous shrinkage resistance.

TABLE 5

	Ex. 15	Ex. 16	Ex. 17	Comp. Ex. 6	Comp. Ex. 7
Block copolymer (A)	Ref. Ex. 12	Ref. Ex. 13	Ref. Ex. 14	Ref. Ex. 15	Ref. Ex. 16
Temperature at which loss tangent value reaches maximum value within a range of from 60 to 110° C.: T (° C.)	75	95	83	83	88
Loss tangent value at temperature T° C.: X	2.79	2.52	1.89	1.02	1.29
Loss tangent value at a temperature of (T - 10)° C.: Y	0.71	0.74	0.66	0.69	0.65
Loss tangent value at a temperature of (T - 30)° C.: Z	0.15	0.13	0.16	0.28	0.29
Loss tangent value at 30° C.	0.06	0.02	0.05	0.11	0.07
Y/X × 100 (%)	25.4	29.4	34.9	67.6	50.4
Z/X × 100 (%)	5.4	5.2	8.5	27.5	22.5
Orienting temperature (° C.)	80	95	85	85	90
Heat shrinkage factor (70° C., 30 sec.) (%)	28	20	23	19	18
Spontaneous shrinkage factor (30° C., 30 days) (%)	1.2	0.5	1.4	3.3	2.7
Cloudiness (%)	1.4	1.2	1.6	1.9	1.6

TABLE 6

	Ex. 18	Ex. 19	Ex. 20	Ex. 21
<u>Blend ratio</u>				
Type	Ref. Ex. 12	Ref. Ex. 12	Ref. Ex. 12	Ref. Ex. 13
wt %	80	60	40	75
Type	Ref. Ex. 13	Ref. Ex. 13	Ref. Ex. 13	Ref. Ex. 15
wt %	20	40	60	25
Temperature at which loss tangent value reaches maximum value within a range of from 60 to 110° C.: T (° C.)	75	75 94	76 95	89
Loss tangent value at temperature T for the highest maximum value: Xmax	2.32	1.52 0.83	0.99 1.38	2.01
Loss tangent value at a temperature of (Tmin - 10)° C.: Y	0.63	0.53	0.46	0.69
Loss tangent value at a temperature of (Tmin - 30)° C.: Z	0.14	0.11	0.08	0.19
Loss tangent value at 30° C.	0.05	0.04	0.03	0.05
Y/Xmax × 100 (%)	27.2	34.9	33.3	34.3
Z/Xmax × 100 (%)	6.0	7.2	5.8	9.5
Orienting temperature (° C.)	82	85	86	96
Heat shrinkage factor (70° C., 30 sec.) (%)	26	24	23	19
Spontaneous shrinkage factor (30° C., 30 days) (%)	1.1	0.9	0.6	0.8
Cloudiness (%)	1.9	2.4	2.2	1.5

Tmin: lowest temperature for maximum value within a temperature range of from 60 to 110° C.

Xmax: highest loss tangent value within a temperature range of from 60 to 110° C.

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TABLE 7

	Ex. 22	Ex. 23
<u>Blend ratio</u>		
Type	Ref. Ex. 13	Ref. Ex. 13
wt %	90	85
Type	Ref. Ex. 11	Ref. Ex. 16
wt %	10	15
Temperature at which loss tangent value reaches maximum value within a range of from 60 to 110° C.: T (° C.)	95	94
Loss tangent value at temperature T for the highest maximum value: Xmax	2.03	1.79
Loss tangent value at a temperature of (Tmin - 10)° C.: Y	0.70	0.61
Loss tangent value at a temperature of (Tmin - 30)° C.: Z	0.15	0.16

TABLE 7-continued

	Ex. 22	Ex. 23
35 Loss tangent value at 30° C.	0.08	0.04
Y/Xmax × 100 (%)	34.4	34.1
Z/Xmax × 100 (%)	7.4	8.9
Orienting temperature (° C.)	97	97
40 Heat shrinkage factor (70° C., 30 sec.) (%)	21	20
Spontaneous shrinkage factor (30° C., 30 days) (%)	0.9	0.7
Cloudiness (%)	2.2	2.1
45 Tmin: lowest temperature for maximum value within a temperature range of from 60 to 110° C.		
Xmax: highest loss tangent value within a temperature range of from 60 to 110° C.		

TABLE 8

	Ex. 24	Ex. 25	Ex. 26	Ex. 27
<u>Blend ratio</u>				
Type	Ref. Ex. 12	Ref. Ex. 12	Ref. Ex. 13	Ref. Ex. 13
wt %	65	50	70	70
Type	GPPS	GPPS	Ref. Ex. 32	Ref. Ex. 32
wt %	34.5	49.5	30	25
Type	E640N	E640N		Ref. Ex. 33
wt %	0.5	0.5		5
Temperature at which loss tangent value reaches maximum value within a range of from 60 to 110° C.: T (° C.)	75 108	77 108	79 95	77 95

TABLE 8-continued

	Ex. 24	Ex. 25	Ex. 26	Ex. 27
Loss tangent value at temperature T for the highest maximum value: Xmax	1.75 0.60	0.57 1.81	0.32 1.72	0.41 1.89
Loss tangent value at a temperature of (Tmin - 10)° C.: Y	0.56	0.34	0.26	0.27
Loss tangent value at a temperature of (Tmin - 30)° C.: Z	0.12	0.09	0.11	0.13
Loss tangent value at 30° C.	0.04	0.03	0.05	0.06
Y/Xmax × 100 (%)	32.0	18.8	15.1	14.3
Z/Xmax × 100 (%)	6.8	5.0	6.4	6.9
Orienting temperature (° C.)	90	93	93	93
Heat shrinkage factor (70° C., 30 sec.) (%)	23	17	25	27
Spontaneous shrinkage factor (30° C., 30 days) (%)	0.9	0.6	0.9	1.1
Cloudiness (%)	2.3	2.2	2.3	2.3

Tmin: lowest temperature for maximum value within a temperature range of from 60 to 110° C.

Xmax: highest loss tangent value within a temperature range of from 60 to 110° C.

TABLE 9

	Ex. 28	Ex. 29
<u>Surface layer and rear layer</u>		
Type	Comp. Ex. 7	Comp. Ex. 7
wt %	99.5	70
Type	E640N	Returned material
wt %	0.5	30
<u>Intermediate layer</u>		
Type	Ex. 19	Ex. 25
wt %	100	70
Type		Returned material
wt %		30
Thickness ratio of surface/intermediate/rear layers	10/80/10	10/80/10
Orienting temperature (° C.)	86	92
Heat shrinkage factor (70° C., 30 sec.) (%)	23	17
Spontaneous shrinkage factor (30° C., 30 days) (%)	1.1	1.1
Cloudiness (%)	2.0	2.8

Returned material: Heat shrinkable multilayer film of Ex. 28 pulverized and then re-extruded

For evaluation of the heat shrinkable (multilayer) film made of the block copolymer (composition) which satisfies conditions regarding the specific molecular structure and molecular weight, the weight average molecular weight of the random copolymer segment of the block copolymer used as a raw material, the weight average molecular weight of the whole and the weight average molecular weight of the polymer component which shows a highest peak after ozonolysis, are shown as Reference Examples in Table 10.

In Tables 11 and 12, Examples wherein the heat shrinkage factor, the spontaneous shrinkage factor and the film formation property of a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, wherein the weight average molecular weights of the random copolymer segment in the block copolymer, the whole and the polymer component which shows a maximum peak after ozonolysis are within specific ranges, the loss tangent value by dynamic viscoelasticity measurement has at least one maximum value within a range of from 60 to 110° C., the loss tangent value at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and the loss tangent value at a temperature lower by 30° C. than the lowest temperature for the maximum value is at most 10% of the highest maximum value, and a heat shrinkable film and a heat shrinkable multilayer film made of the specific composition, were measured, are shown.

From the values shown in Tables 11 and 12, it is found that the block copolymer which satisfies the weight average molecular weight of the molecules and the conditions of the dynamic viscoelasticity behaviors, and the heat shrinkable film and the heat shrinkable multilayer film made of the specific composition, satisfy favorable film formation property while they have favorable heat shrinkability and spontaneous shrinkage resistance.

Further, from values shown in Tables 11 and 12, it is found that the heat shrinkable film and the heat shrinkable multilayer film made of a composition comprising block copolymers having a difference in temperature for the maximum and the highest loss tangent value of at least 3° C., selected among the block copolymers which show specific dynamic viscoelasticity behaviors, have a wide range of the temperature for film formation and satisfy favorable film formation property, while they have favorable heat shrinkability and spontaneous shrinkage resistance.

TABLE 10

	Ref. Ex. 17	Ref. Ex. 18	Ref. Ex. 19	Ref. Ex. 20	Ref. Ex. 21
Weight average molecular weight of random copolymer segment contained in a block comprising a conjugated diene and a vinyl aromatic hydrocarbon: MB (ten thousand)	9.10	7.60	23.7	13.8	6.40

TABLE 10-continued

	Ref. Ex. 17	Ref. Ex. 18	Ref. Ex. 19	Ref. Ex. 20	Ref. Ex. 21
Weight average molecular weight of block copolymer: M (ten thousand)	18.3	12.1	27.8	18.2	13.5
Weight average molecular weight of polymer which shows a highest peak in GPC measurement after ozonolysis: M' (ten thousand)	5.87	2.76	3.09	2.70	5.12
M' /M	0.32	0.23	0.11	0.15	0.38

TABLE 11

	Ex. 30	Ex. 31	Ex. 32	Ex. 33	Ex. 34
<u>Blend</u>					
Type	Ref. Ex. 17	Ref. Ex. 18	Ref. Ex. 19	Ref. Ex. 20	Ref. Ex. 21
wt %	100	100	100	100	100
Lowest temperature at which loss tangent value reaches maximum value within a range of from 60 to 110° C.: T (° C.)	88.8	86.6	95.2	74.7	87.9
Highest maximum value of loss tangent value: Xmax	2.10	2.50	2.61	2.28	2.13
Loss tangent value at a temperature of (T - 10)° C.: Y	0.73	0.57	0.75	0.69	0.69
Loss tangent value at a temperature of (T - 30)° C.: Z	0.10	0.11	0.14	0.05	0.10
Y/Xmax × 100 (%)	34.7	22.8	28.7	30.3	32.4
Z/Xmax × 100 (%)	4.76	4.40	5.36	2.19	4.69
<u>Heat shrinkage factor</u>					
Orienting temperature (° C.)	90	88	96	76	90
Shrinkage factor (%; 70° C., 30 sec.)	21	20	24	22	19
Spontaneous shrinkage factor (%; 30° C., 30 days)	0.7	0.8	0.9	1.1	0.7
Film formation property (occurrence of failure in outer appearance such as wrinkles or dry scaly skin)	○	○	○	○	○

TABLE 12

	Ex. 35	Ex. 36	Ex. 37	Ex. 38	Ex. 39
<u>Blend</u>					
Type	Ref. Ex. 17	Ref. Ex. 18	Ref. Ex. 18	Ref. Ex. 21	Ref. Ex. 21
wt %	33	33	67	70	70
Type	Ref. Ex. 21	Ref. Ex. 19	GPPS	Ref. Ex. 32	Ref. Ex. 32
wt %	67	67	33	30	25
Type			E640N		Ref. Ex. 33
wt %			0.5		5
Lowest temperature at which loss tangent value reaches maximum value within a range of from 60 to 110° C.: T (° C.)	88.2	91.8	87.0	88.5	89.3
Highest maximum value of loss tangent value: Xmax	2.13	2.51	1.72	1.55	1.51
Loss tangent value at a temperature of (T - 10)° C.: Y	0.53	0.77	0.65	0.57	0.53
Loss tangent value at a temperature of (T - 30)° C.: Z	0.10	0.15	0.13	0.09	0.09
Y/Xmax × 100 (%)	24.9	30.7	37.8	36.8	35.1
Z/Xmax × 100 (%)	4.69	5.98	7.56	5.81	5.96
<u>Heat shrinkage factor</u>					
Orienting temperature (° C.)	90	90	96	93	93
Shrinkage factor (%; 70° C., 30 sec.)	21	22	16	17	17

TABLE 12-continued

	Ex. 35	Ex. 36	Ex. 37	Ex. 38	Ex. 39
Spontaneous shrinkage factor (%, 30° C., 30 days)	0.7	0.8	0.5	0.5	0.7
Film formation property (occurrence of failure in outer appearance such as wrinkles or dry scaly skin)	○	○	○	○	○

For evaluation of the heat shrinkable (multilayer) film made of block copolymer compositions having different dynamic viscoelasticity behaviors to the temperature, the temperature at which the loss tangent value of the block copolymer used as a raw material reaches the maximum and highest value, the loss tangent value at a temperature lower by 10° C. than the temperature for the highest value and its proportion to the highest value, and the loss tangent value at a temperature lower by 30° C. and its proportion to the highest value, are shown as Reference Examples in Table 13. As evident from this Table, it is found that the dynamic viscoelasticity behaviors of each of the block copolymers of Reference Examples are within specific ranges relative to a temperature change.

In Tables 14 to 16, the combination and the formulation proportion of block copolymers having different dynamic viscoelasticity behaviors to the temperature, and the difference in temperature at which the loss tangent value of each of the block copolymer components reaches the highest and maximum value, are shown and further, Examples wherein the heat shrinkage factor and the spontaneous shrinkage factor of a heat shrinkable film and a heat shrinkable multilayer film were measured while changing the orienting temperature are shown, and Comparative Examples are also shown.

By comparison of values in Tables 14 to 16, it is found that the heat shrinkable film and the heat shrinkable multi-

layer film made of a composition comprising block copolymers having a difference in temperature at which the loss tangent value reaches the maximum and highest value of at least 3° C., selected among the block copolymers which show specific dynamic viscoelasticity behaviors, have a wide range of the temperature for film formation and satisfy favorable film formation property, while they have favorable heat shrinkability and spontaneous shrinkage resistance.

TABLE 13

	Ref. Ex. 22	Ref. Ex. 23
Temperature at which loss tangent value reaches the maximum and highest value: T (° C.)	92.6	81.2
Highest loss tangent value at temperature T: X	2.42	2.76
Loss tangent value at a temperature lower by 10° C. than temperature T: Y	0.752	0.612
Loss tangent value at a temperature lower by 30° C. than temperature T: Z	0.1440	0.0452
Y/X × 100 (%)	31.1	22.2
Z/X × 100 (%)	5.95	1.64

TABLE 14

	Ex. 40	Ex. 41	Ex. 42	Ex. 43	Ex. 44	Ex. 45	Ex. 46	Ex. 47
Block copolymer (A) (i)	Ref. Ex. 12	Ref. Ex. 12	Ref. Ex. 4	Ref. Ex. 4	Ref. Ex. 1	Ref. Ex. 22	Ref. Ex. 1	Ref. Ex. 23
Block copolymer (A) or (A2) (ii)	Ref. Ex. 22	Ref. Ex. 4	Ref. Ex. 22	Ref. Ex. 9	Ref. Ex. 4	Ref. Ex. 3	Ref. Ex. 3	Ref. Ex. 3
Vinyl aromatic hydrocarbon polymer (B) (iii)							E640N	
Copolymers blended	(i):(ii)	(i):(ii)	(i):(ii)	(i):(ii)	(i):(ii)	(i):(ii)	(i):(ii)	(i):(ii)
Weight ratio	30:70	60:40	30:70	70:30	30:70	70:30	70:29:1	60:40
Difference in temperature at which loss tangent value reaches the highest and maximum value T(ii) - T(i) (° C.)	17.6	9.6	8.0	23.4	4.1	12.4	24.5	23.8
Heat shrinkage factor at 70° C. for 30 sec. (%)								
Orienting temperature								
87° C.	27	28	25	22	25	20	22	22
90° C.	24	28	22	19	21	18	20	20
93° C.	20	18	18	15	19	16	16	18
96° C.	18	15	15	12	16	12	12	17
Spontaneous shrinkage factor (30° C., 30 days) (%)	0.8	1.0	0.7	0.9	0.9	1.2	1.0	0.9

Spontaneous shrinkage factor: Measured by using a film oriented at 90° C.



TABLE 15

	Comp. Ex. 8
Block copolymer (A) (i)	
Block copolymer (A2) (ii)	Ref. Ex. 9
Block copolymer (A2) or another (iii)	Ref. Ex. 15
Copolymers blended	(ii):(iii)
Weight ratio	30:70
Difference in temperature at which loss tangent value reaches the highest and maximum value	24.8
T(ii) - T(i) or T(ii) - T(iii) or T(iii) - T(i) (° C.)	
Heat shrinkage factor at 70° C. for 30 sec. (%)	
Orienting temperature	
87° C.	24
90° C.	21
93° C.	18
96° C.	15
Spontaneous shrinkage factor (30° C., 30 days) (%)	2.8

Spontaneous shrinkage factor: Measured by using a film oriented at 90° C.

TABLE 16

	Ex. 48	Ex. 49	Ex. 50	Ex. 51
<u>Surface layer and rear layer</u>				
Blended resin (iv)	730L	Ex. 40	Ref. Ex. 32	730L
Blended resin (v)	E640N		Ref. Ex. 33	Returned material
Blended ratio (iv):(v)	99:1	100:0	70:30	70:30
<u>Intermediate layer</u>				
Blended resin (vi)	Ex. 40	730L	Ex. 40	Ex. 40
Blended resin (vii)			Ref. Ex. 32	Returned material
Blended ratio (vi):(vii)	100:0	100:0	90:10	70:30
Thickness ratio of surface/intermediate /rear layers	10/80/10	10/80/10	10/80/10	10/80/10
Heat shrinkage factor at 70° C. for 30 sec. (%)				
Orienting temperature				
87° C.	26	22	26	25
90° C.	22	20	21	22
93° C.	19	18	19	18
96° C.	18	16	18	17
Spontaneous shrinkage factor (30° C., 30 days) (%)	0.9	1.4	1.0	1.0

Spontaneous shrinkage factor: Measured by using a film oriented at 90° C.  
Returned material: Heat shrinkable multilayer film of Ex. 51 pulverized and then re-extruded

For evaluation of the heat shrinkable (multilayer) film made of block copolymer compositions having different weight average molecular weights, the temperature at which the loss tangent value of the block copolymer used as a part of raw materials reaches the maximum and highest value, the loss tangent value at a temperature lower by 10° C. than the temperature for the highest value and its proportion to the highest value, and the loss tangent value at a temperature lower by 30° C. and its proportion to the highest value, are shown as Reference Examples in Table 17. From this Table, it is found that the dynamic viscoelasticity behaviors of each of the block copolymers in Reference Examples are within specific ranges relative to the temperature change.

The dynamic viscoelasticity behaviors of the composition composed mainly of block copolymers having different

weight average molecular weights, and the outer appearance at the time of film formation, the heat shrinkage factor and the spontaneous shrinkage factor of a heat shrinkable (multilayer) film formed by orientation while changing the temperature, were measured and are shown in Tables 18 to 21 as Examples.

From the results shown in Tables 18 to 21, it is found that the composition of the block copolymers which have a certain difference in the weight average molecular weight and which satisfy the standards of the dynamic viscoelasticity, is excellent in spontaneous shrinkability while it has favorable film formation property and low temperature heat shrinkability.

TABLE 17

	Ref. Ex. 24	Ref. Ex. 26	Ref. Ex. 29	Ref. Ex. 30
Temperature at which loss tangent value reaches the maximum and highest value: T (° C.)	74.6	73.1	105.1	78.5
Highest loss tangent value at temperature T: X	2.74	2.61	2.37	2.68

TABLE 17-continued

	Ref. Ex. 24	Ref. Ex. 26	Ref. Ex. 29	Ref. Ex. 30
Loss tangent value at a temperature lower by 10° C. than temperature T: Y	0.524	0.507	0.563	0.518
Loss tangent value at a temperature lower by 30° C. than temperature T: Z	0.0860	0.0819	0.123	0.0834
Y/X × 100 (%)	19.1	19.4	23.8	19.3
Z/X × 100 (%)	3.14	3.14	5.19	3.11

TABLE 18

	Ex. 52	Ex. 53	Ex. 54	Ex. 55	Ex. 56	Ex. 57
Block copolymer (A)	Ref. Ex. 24	Ref. Ex. 26	Ref. Ex. 24	Ref. Ex. 29	Ref. Ex. 30	Ref. Ex. 24
Weight average molecular weight of (A) (Mw1)	204,000	151,000	204,000	182,000	252,000	204,000
Block copolymer (A3)	Ref. Ex. 25	Ref. Ex. 27	Ref. Ex. 25	Ref. Ex. 25	Ref. Ex. 31	Ref. Ex. 25
Weight average molecular weight of (A3) (Mw2)	127,000	119,000	127,000	127,000	49,000	127,000
Blend ratio of (A) to (A3) by weight (A):(A3)	70:30	70:30	70:30	30:70	70:30	70:30
Mw2/Mw1	0.62	0.79	0.62	0.70	0.19	0.62
Temperature at which loss tangent value reaches a maximum value at a temperature of at least 60° C.: T(° C.)	79	84	79	92	85	79
Loss tangent value at temperature T: X	2.5	2.5	2.5	2.3	2.3	2.5
Loss tangent value at a temperature lower by 10° C. than temperature T: Y	0.74	0.72	0.74	0.80	0.84	0.74
Loss tangent value at a temperature lower by 30° C. than temperature T: Z	0.14	0.14	0.14	0.14	0.19	0.14
Y/X × 100 (%)	29.6	28.8	29.6	34.8	36.5	29.6
Z/X × 100 (%)	5.6	5.6	5.6	6.1	8.3	5.6
Vinyl aromatic hydrocarbon polymer composition (B)						
Type of resin/blend ratio based on 100 parts by weight of compositions (A) and (A3)	Nil	Nil	GPPS/10	Nil	Nil	Ref. Ex. 32/10 HIPS/1

TABLE 19

	Comp. Ex. 9	Comp. Ex. 10	Comp. Ex. 11	Comp. Ex. 12
Block copolymer (A)	Ref. Ex. 26	Ref. Ex. 24	Ref. Ex. 26	Ref. Ex. 26
Weight average molecular weight of (A) (Mw1)	151,000	204,000	151,000	151,000
Block copolymer (A3)	Ref. Ex. 28	Ref. Ex. 25	Ref. Ex. 27	Ref. Ex. 27
Weight average molecular weight of (A3) (Mw2)	139,000	127,000	119,000	119,000
Blend ratio of (A) to (A3) by weight (A):(A3)	70:30	95:5	30:70	5:95
Mw2/Mw1	0.92	0.62	0.79	0.79
Temperature at which loss tangent value reaches a maximum value at a temperature of at least 60° C.: T(° C.)	77	77	94	100
Loss tangent value at temperature T: X	2.7	2.6	2.1	1.9
Loss tangent value at a temperature lower by 10° C. than temperature T: Y	0.65	0.75	0.88	0.97
Loss tangent value at a temperature lower by 30° C. than temperature T: Z	0.13	0.15	0.19	0.21
Y/X × 100 (%)	24.1	28.8	41.9	51.1
Z/X × 100 (%)	4.8	5.8	9.0	11.1
Vinyl aromatic hydrocarbon polymer composition (B)				
Type of resin/blend ratio based on 100 parts by weight of compositions (A) and (A3)	Nil	Nil	Nil	Nil

TABLE 20

	Ex. 52	Ex. 53	Ex. 54	Ex. 55	Ex. 56	Ex. 57
Heat shrinkage factor at 70° C. for 30 sec. (%)	78° C. X	X	X		X	X
	81° C. 32/Δ	33/Δ	30/Δ		29/Δ	28/Δ
	84° C. 26/○	28/○	24/○	X	24/○	25/○

TABLE 20-continued

	Ex. 52	Ex. 53	Ex. 54	Ex. 55	Ex. 56	Ex. 57
Film formation property (outer appearance of oriented film)	87° C. 23/○ 90° C. 20/○ 93° C. X 96° C. X 99° C. 102° C.	23/○ 20/○ 18/○ X	22/○ 20/○ X	29/Δ 24/○ 22/○ 19/○ 16/○ X	19/○ 13/○ 10/○ X	23/○ 19/○ X
Orienting temperature (° C.)	84	84	84	90	84	84
Spontaneous shrinkage factor (%)	0.7	1.2	0.7	1.2	1.1	0.7

TABLE 21

	Comp. Ex. 9	Comp. Ex. 10	Comp. Ex. 11	Comp. Ex. 12
Orienting temperature				
Heat shrinkage factor at 70° C. for 30 sec. (%)	78° C. X 81° C. 30/Δ 84° C. 26/Δ	X 28/Δ 24/Δ		
Film formation property (outer appearance of oriented film)	87° C. 22/Δ 90° C. X 93° C. 96° C. 99° C. 102° C.	20/Δ 15/Δ X	25/Δ 18/○ 16/○ 13/○ 10/○ X	X 20/Δ 14/○ 10/○ 8/○ X
Orienting temperature (° C.)	84	84	90	93
Spontaneous shrinkage factor (%)	0.7	0.7	1.8	3.6

TABLE 22

	CLEAREN 730L*
Weight average molecular weight of (A) (Mw1)	180,000
Weight average molecular weight of (B) (Mw2)	70,000
Mw2/Mw1	0.39
Temperature at which loss tangent value reaches a maximum value at a temperature of at least 60° C.: T(° C.)	107
Loss tangent value at temperature T: X	1.5
Loss tangent value at a temperature lower by 10° C. than temperature T: Y	0.59
Loss tangent value at a temperature lower by 30° C. than temperature T: Z	0.19
Y/X × 100 (%)	39.3
Z/X × 100 (%)	12.7

\*Lot 900315

## Industrial Applicability

The block copolymer wherein the loss tangent value obtained by dynamic viscoelasticity measurement has a specific relation to the temperature, and the heat shrinkable (multilayer) film composed mainly of the copolymer composition containing the block copolymer as an essential component of the present invention, have remarkably improved spontaneous shrinkage resistance without their original heat shrinkability being impaired, and are suitable for e.g. a heat shrinkable label, a heat shrinkable cap seal, a protective film for bottles, a pack guard shrink packaging, or an electrical insulating coating for e.g. capacitors and dry batteries.

What is claimed is:

1. A block copolymer (A) comprising a vinyl aromatic hydrocarbon and a conjugated diene, wherein the relation of

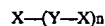
the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature satisfies the following conditions:

- (1) there is at least one maximum value within a temperature range of from 60 to 110° C.,
- (2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and
- (3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value.

2. The block copolymer (A) according to claim 1, wherein in the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, there is at least one maximum value within a temperature range of from 65 to 100° C., and the conditions (2) and (3) defined are satisfied.

3. The block copolymer (A) according to claim 1, wherein in the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, the highest maximum value of loss tangent within a temperature range of from 60 to 110° C. is within a range of from 0.5 to 4.0, and the loss tangent value at 30° C. is within a range of at least 0.01 and less than 0.4.

4. The block copolymer (A) according to claim 1, wherein the molecular structure is represented by the following formula, its weight average molecular weight is from 100,000 to 300,000, and the following conditions (a) to (c) are satisfied:



wherein n is an integer of at least 1:

- (a) X is a block having a chain comprising one type or at least two types of vinyl aromatic hydrocarbons,
- (b) Y is a block containing at least one random copolymer segment of a conjugated diene and a vinyl aromatic

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hydrocarbon, each being of one type or at least two types, having a weight average molecular weight of from 40,000 to 250,000, and

- (c) when a molecular weight distribution of a polymer mixture comprising a vinyl aromatic hydrocarbon obtained by ozonolysis of the block copolymer is measured, the relation between the weight average molecular weight ( $M_w$ ) of the polymer component showing the highest peak and the weight average molecular weight ( $M_w$ ) of the block copolymer before the treatment is  $0.1 \leq M_w/M_w \leq 0.4$ .

5. A block copolymer composition containing at least two types of the different block copolymers (A) which satisfy the conditions as defined in claim 1.

6. A block copolymer composition containing at least two types of the different block copolymers (A) which satisfy the conditions as defined in claim 1, wherein the relation of the loss tangent value obtained by dynamic viscoelasticity measurement of the composition to the temperature satisfies conditions (1) there is at least one maximum value within a temperature range of from 60 to 110° C., (2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and (3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value.

7. A block copolymer composition containing at least two types of the different block copolymers (A) which satisfy the conditions as defined in claim 4, wherein the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature satisfies conditions (1) there is at least one maximum value within a temperature range of from 60 to 110° C., (2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and (3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value.

8. A block copolymer composition containing the block copolymer (A) as defined in claim 1 and a vinyl aromatic hydrocarbon polymer containing at least one member selected from the following polymers (B1) to (B3):

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A)),

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

9. A block copolymer composition containing the block copolymer (A) as defined in claim 1 and a vinyl aromatic hydrocarbon polymer containing at least one member selected from the following polymers (B1) to (B3), wherein the relation of the loss tangent value obtained by dynamic viscoelasticity measurement of the composition to the temperature satisfies the conditions (1) to (3) defined:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A)),

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(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

10. A block copolymer composition comprising a composition of the block copolymer (A) as defined in claim 1 and the following block copolymer (A2) in a compositional ratio by weight of  $0.1 \leq A/(A+A2) \leq 0.95$ :

the block copolymer (A2) is a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene, wherein in the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, there is at least one maximum value within a temperature range of from 63 to 120° C., and the lowest temperature for the maximum value of the loss tangent value within said range is higher by at least 3° C. than the lowest temperature for the maximum value of the loss tangent value of the block copolymer (A).

11. A block copolymer composition comprising a composition of the block copolymer (A) as defined in claim 1 and the following block copolymer (A2) in a compositional ratio by weight of  $0.1 \leq A/(A+A2) \leq 0.95$ , wherein the relation of the loss tangent value obtained by dynamic viscoelasticity measurement of the composition to the temperature satisfies the conditions (1) to (3) defined:

the block copolymer (A2) is a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene, wherein in the relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature, there is at least one maximum value within a temperature range of from 63 to 120° C., and the lowest temperature for the maximum value of the loss tangent value within said range is higher by at least 3° C. than the lowest temperature for the maximum value of the loss tangent value of the block copolymer (A).

12. A composition containing the block copolymer composition as defined in claim 10 and at least one vinyl aromatic hydrocarbon polymer selected from the following polymers (B1) to (B3) in an amount of at most 100 parts by weight based on 100 parts by weight of the block copolymer composition:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A) and the block copolymer (A2)),

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

13. A composition containing the block copolymer composition as defined in claim 10 and at least one vinyl aromatic hydrocarbon polymer selected from the following

polymers (B1) to (B3) in an amount of at most 100 parts by weight based on 100 parts by weight of the block copolymer composition, wherein the relation of the loss tangent value obtained by dynamic viscoelasticity measurement of the composition to the temperature satisfies conditions (1) there is at least one maximum value within a temperature range of from 60 to 110° C., (2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and (3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A) and the block copolymer (A2)),

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

14. A block copolymer composition comprising the block copolymer (A) comprising a vinyl aromatic hydrocarbon and a conjugated diene as defined in claim 1 and having a weight average molecular weight  $Mw1$  within a range of  $100,000 \leq Mw1 \leq 300,000$ , and a block copolymer (A3) comprising a vinyl aromatic hydrocarbon and a conjugated diene and having a weight average molecular weight  $Mw2$  in relation to  $Mw1$  within a range of  $0.1 \leq Mw2/Mw1 \leq 0.85$ , wherein the compositional ratio by weight of (A) to (A3) is within a range of  $0.1 < A/(A+A3) < 0.9$ .

15. A block copolymer composition comprising the block copolymer (A) comprising a vinyl aromatic hydrocarbon and a conjugated diene as defined in claim 1 and having a weight average molecular weight  $Mw1$  within a range of  $100,000 \leq Mw1 \leq 300,000$ , and a block copolymer (A3) comprising a vinyl aromatic hydrocarbon and a conjugated diene and having a weight average molecular weight  $Mw2$  in relation to  $Mw1$  within a range of  $0.1 \leq Mw2/Mw1 \leq 0.85$ , wherein the compositional ratio by weight of (A) to (A3) is within a range of  $0.1 < A/(A+A3) < 0.9$ , and wherein the relation of the loss tangent value obtained by dynamic viscoelasticity measurement of the composition to the temperature satisfies conditions (1) there is at least one maximum value within a temperature range of from 60 to 110° C., (2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and (3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value.

16. A composition containing the block copolymer composition as defined in claim 4 and a vinyl aromatic hydrocarbon polymer containing at least one of the following (B1) to (B3) in an amount of at most 100 parts by weight based on 100 parts by weight of the block copolymer composition:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A) and the block copolymer (A3)),

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic

hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

17. A composition containing the block copolymer composition as defined in claim 8 and a vinyl aromatic hydrocarbon polymer containing at least one of the following (B1) to (B3) in an amount of at most 100 parts by weight based on 100 parts by weight of the block copolymer composition, wherein the relation of the loss tangent value obtained by dynamic viscoelasticity measurement of the composition to the temperature satisfies conditions (1) there is at least one maximum value within a temperature range of from 60 to 110° C., (2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and (3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A) and the block copolymer (A3)),

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (A) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

18. A film or sheet made of the block copolymer or the copolymer composition as defined in claim 1.

19. A heat shrinkable film made of the block copolymer or the block copolymer composition as defined in claim 1.

20. A heat shrinkable film obtained by orienting the film or sheet as defined in claim 18.

21. A multilayer film or multilayer sheet having at least one layer made of the block copolymer or the copolymer composition as defined in claim 1.

22. A heat shrinkable multilayer film employing the block copolymer or the block copolymer composition as defined in claim 8 for at least one layer.

23. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 21.

24. A multilayer film or multilayer sheet having a layer containing the block copolymer (A) as defined in claim 5, as a surface layer, and a layer formed by a vinyl aromatic hydrocarbon polymer containing at least one member selected from the following polymers (B1) to (B3), as a layer other than the surface layer:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A)),

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of

23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

25. A multilayer film or multilayer sheet having a layer formed by a vinyl aromatic hydrocarbon polymer containing at least one member selected from the following polymers (B1) to (B3), as a surface layer, and a layer containing the block copolymer (A) as defined in claim 5, as a layer other than the surface layer:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene (excluding the block copolymer (A)),

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

26. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 24.

27. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 25.

28. A multilayer film or multi layer sheet having at least one layer obtained by mixing 100 parts by weight of a composition composed mainly of a block copolymer (A), with at most 50 parts by weight (0 part by weight not included) of a resin mixture forming the multilayer film or multilayer sheet and/or the heat shrinkable multilayer film as defined in claim 23, said block copolymer (A) comprising a vinyl aromatic hydrocarbon and a conjugated diene, and having a relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature which satisfies the following conditions (1) to (3):

- (1) there is at least one maximum value within a temperature range of from 60 to 110° C.,
- (2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and
- (3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value.

29. A multilayer film or multilayer sheet obtained by mixing 100 parts by weight of a vinyl aromatic hydrocarbon polymer containing at least one member selected from the following polymers (B1) to (B3) with at most 50 parts by weight (0 part by weight not included) of a resin mixture forming the multilayer film or multilayer sheet and/or the heat shrinkable multilayer film as defined in claim 23:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene,

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a

refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

30. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 28.

31. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 29.

32. A method for producing the block copolymer (A) as defined in claim 1, which comprises a step of adding a vinyl aromatic hydrocarbon and/or a conjugated diene as a monomer as mixed or separately, simultaneously, and intermittently or continuously, to the reaction system so that the feed rate of the monomer is substantially lower than the polymerization reaction rate, to polymerize the random copolymer segment, in anionic polymerization employing an organic lithium compound as the polymerization initiator in an organic solvent.

33. A method for producing the block copolymer (A) as defined in claim 1, which comprises a step of adding a vinyl aromatic hydrocarbon and/or a conjugated diene as a monomer as mixed or separately, simultaneously, and intermittently or continuously, in the presence of a randomizing agent to polymerize the random copolymer segment, in anionic polymerization employing an organic lithium compound as the polymerization initiator in an organic solvent.

34. A film or sheet made of the block copolymer or the copolymer composition as defined in claim 5.

35. A film or sheet made of the block copolymer or the copolymer composition as defined in claim 8.

36. A heat shrinkable film made of the block copolymer or the block copolymer composition as defined in claim 5.

37. A heat shrinkable film made of the block copolymer or the block copolymer composition as defined in claim 8.

38. A heat shrinkable film obtained by orienting the film or sheet as defined in claim 34.

39. A heat shrinkable film obtained by orienting the film or sheet as defined in claim 35.

40. A multilayer film or multilayer sheet having at least one layer made of the block copolymer or the copolymer composition as defined in claim 5.

41. A multilayer film or multilayer sheet having at least one layer made of the block copolymer or the copolymer composition as defined in claim 8.

42. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 40.

43. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 41.

44. A multilayer film or multilayer sheet having at least one layer obtained by mixing 100 parts by weight of a composition composed mainly of a block copolymer (A), with at most 50 parts by weight (0 part by weight not included) of a resin mixture forming the multilayer film or multilayer sheet and/or the heat shrinkable multilayer film as defined in claim 42, said block copolymer (A) comprising a vinyl aromatic hydrocarbon and a conjugated diene, and having a relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature which satisfies the following conditions (1) to (3):

- (1) there is at least one maximum value within a temperature range of from 60 to 110° C.,
- (2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and

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(3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value.

45. A multilayer film or multilayer sheet having at least one layer obtained by mixing 100 parts by weight of a composition composed mainly of a block copolymer (A), with at most 50 parts by weight (0 part by weight not included) of a resin mixture forming the multilayer film or multilayer sheet and/or the heat shrinkable multilayer film as defined in claim 43, said block copolymer (A) comprising a vinyl aromatic hydrocarbon and a conjugated diene, and having a relation of the loss tangent value obtained by dynamic viscoelasticity measurement to the temperature which satisfies the following conditions (1) to (3):

(1) there is at least one maximum value within a temperature range of from 60 to 110° C.,

(2) the value of loss tangent at a temperature lower by 10° C. than the lowest temperature for the maximum value is at most 40% of the highest maximum value, and

(3) the value of loss tangent at a temperature lower by 30° C. than the lowest temperature is at most 10% of the highest maximum value.

46. A multilayer film or multilayer sheet obtained by mixing 100 parts by weight of a vinyl aromatic hydrocarbon polymer containing at least one member selected from the following polymers (B1) to (B3) with at most 50 parts by weight (0 part by weight not included) of a resin mixture forming the multilayer film or multilayer sheet and/or the heat shrinkable multilayer film as defined in claim 42:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene,

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature

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of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

47. A multilayer film or multilayer sheet obtained by mixing 100 parts by weight of a vinyl aromatic hydrocarbon polymer containing at least one member selected from the following polymers (B1) to (B3) with at most 50 parts by weight (0 part by weight not included) of a resin mixture forming the multilayer film or multilayer sheet and/or the heat shrinkable multilayer film as defined in claim 43:

(B1) a vinyl aromatic hydrocarbon polymer,

(B2) a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene,

(B3) a rubber-modified transparent resin which is a composition of a copolymer (a) comprising a vinyl aromatic hydrocarbon and a (meth)acrylate and having a refractive index of from 1.550 to 1.580 at a temperature of 23° C., and a rubber-like elastic body (b) having a refractive index of from 1.535 to 1.550 at a temperature of 23° C., wherein the copolymer (a) forms a continuous phase and the rubber-like elastic body (b) forms a disperse phase, and the weight ratio is (a)/(b)=60/40 to 97/3.

48. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 44.

49. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 45.

50. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 46.

51. A heat shrinkable multilayer film obtained by orienting the multilayer film or multilayer sheet as defined in claim 47.

\* \* \* \* \*



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**Kobashi et al.**(54) **STYRENIC RESIN COMPOSITION****Publication Classification**(75) Inventors: **Kazunori Kobashi**, Sakura-shi (JP);  
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Tokyo (JP)(57) **ABSTRACT**(21) Appl. No.: **10/543,402**(22) PCT Filed: **Jan. 23, 2004**(86) PCT No.: **PCT/JP04/00588**

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Surface impact strength in a molded article of an impact-resistant styrene resin composition, and balance between the surface impact strength and the rigidity is improved. Disclosed is a styrene resin composition comprising a styrene copolymer (A), and a block copolymer (B) comprising a polymer block (b1) of a styrene monomer and a polymer block (b2) of a conjugated diene monomer, wherein the styrene copolymer (A) is a copolymer of a styrene monomer (a), a butyl acrylate (b) and a methyl methacrylate (c), the block copolymer (B) forms a multi-layered structure in which a layer of the polymer block (b1) and a layer of the polymer block (b2) of the diene monomer are alternately laminated, and the styrene resin composition has 9 to 25%, on a weight basis, of structural units derived from the conjugated diene monomer.



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FIG. 1

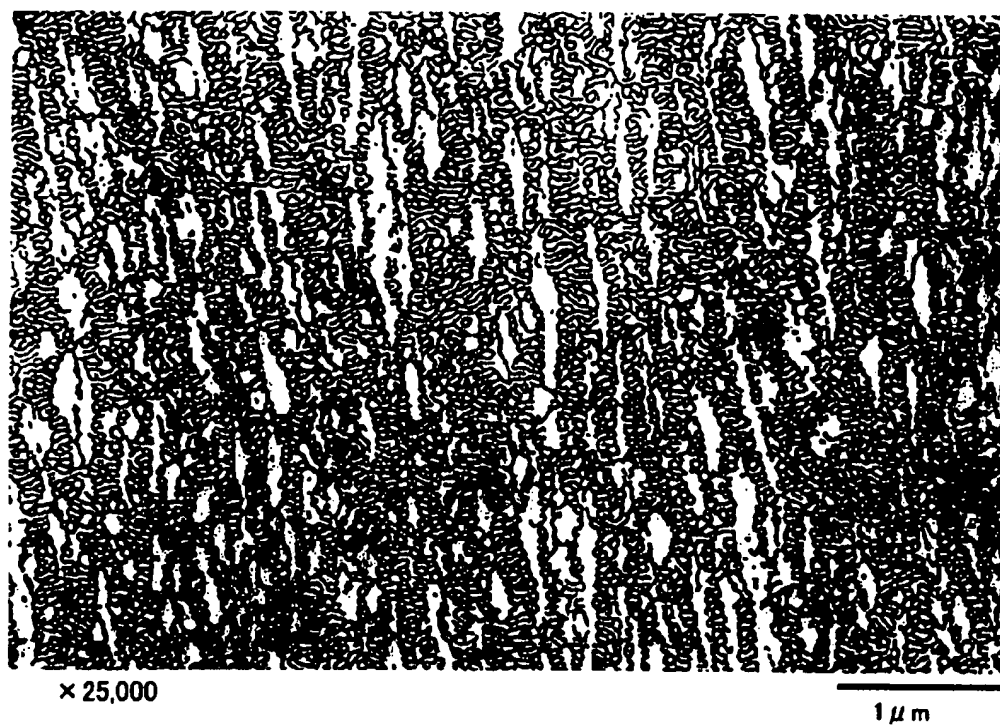


FIG. 2

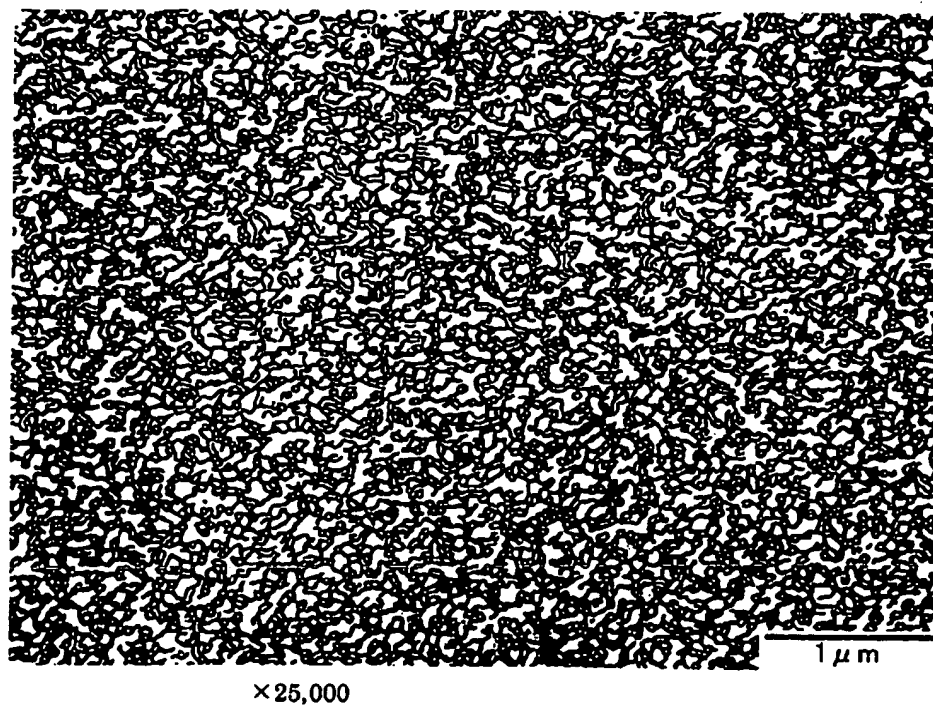
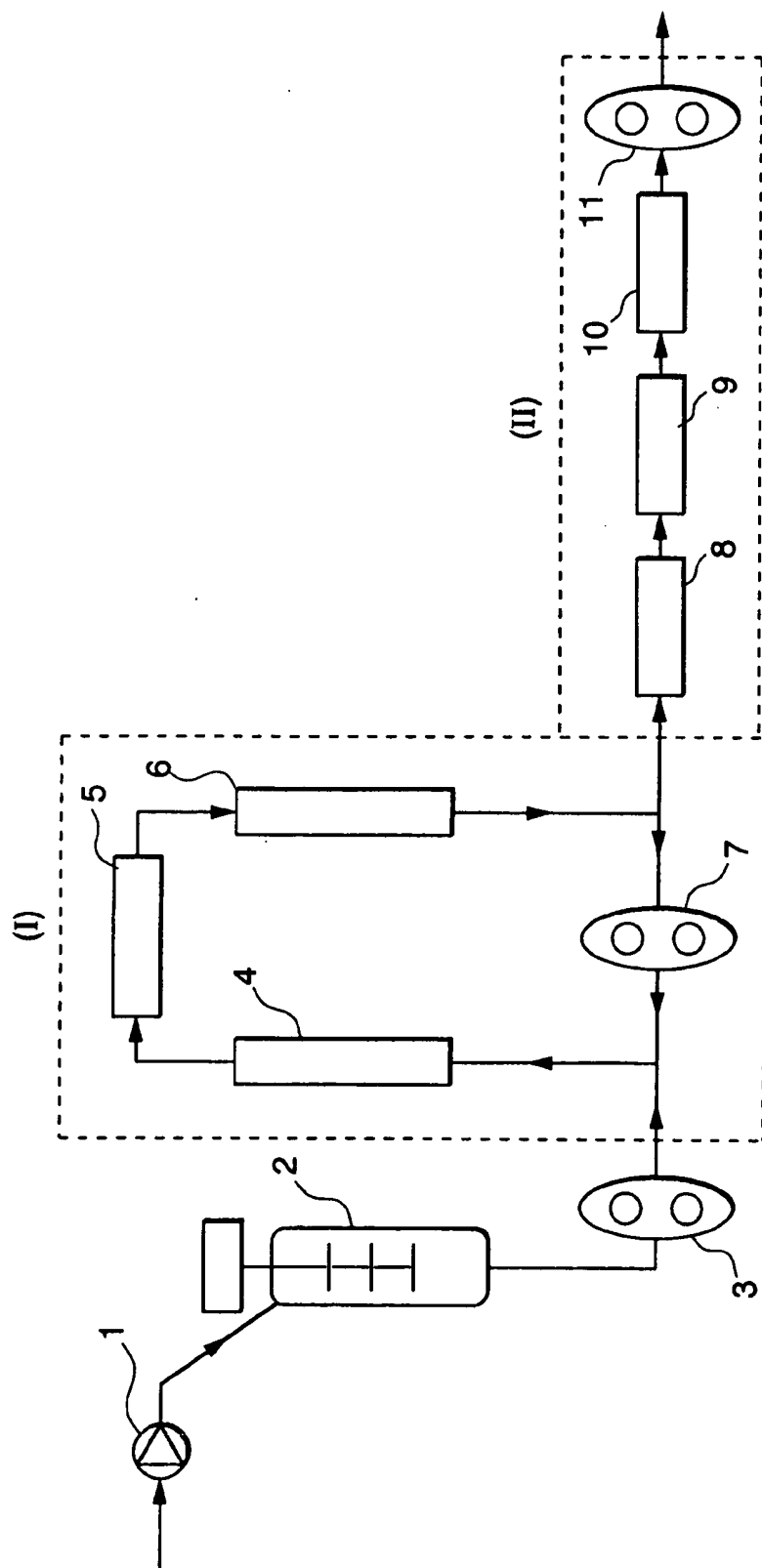


FIG. 3



## STYRENIC RESIN COMPOSITION

### TECHNICAL FIELD

[0001] The present invention relates to a novel styrene resin composition obtained by mixing a styrene resin with a thermoplastic elastomer.

### BACKGROUND ART

[0002] Styrene resins have been widely used for plastic containers because of superior formability. Taking into account problems such as effects on the environment, vinyl chloride resins have recently been replaced by styrene resins in the field of plastic containers, and a so-called impact-resistant styrene resin composition obtained by mixing a styrene resin with a thermoplastic elastomer has been widely used in forming sheets obtained by vacuum molding and press forming the styrene resin sheets. However, increase in the content of the thermoplastic elastomer in an impact-resistant styrene resin composition leads to reduction in the rigidity of the forming sheet, although the impact resistance thereof is enhanced, and makes the resulting molded article subject to deformation when high loads are applied from the outside, thereby tending to cause damage of goods contained inside in the case of a container for packing the goods. On the other hand, when the content of the thermoplastic elastomer in the impact-resistant styrene resin composition is decreased, the molded article has low impact strength, although the rigidity is enhanced, and thus the molded article is likely to crack, fracture, and break. Therefore, there have been attempts to achieve good balance between the rigidity and the impact resistance, which conflict with each other. For example, there has been known a transparent impact-resistant resin composition comprising a styrene-butadiene block copolymer containing 65 to 85% by weight of a styrene block, and a styrene-butyl acrylate copolymer, and a styrene-butadiene block copolymer containing 10 to 50% by weight of a styrene block (see, for example, Japanese Patent Application, First Publication No. Hei 7-309992).

[0003] Although the transparent impact-resistant resin composition can impart excellent rigidity and excellent impact resistance to a molded article of the composition, the resulting molded article has insufficient surface impact strength, and various secondarily formed articles such as blister packs, carrier tapes and containers for food obtained by secondarily forming a forming sheet are likely to break and crack by vibration upon dropping or transportation when containing goods.

### DISCLOSURE OF INVENTION

[0004] Objects of the present invention are to remarkably improve surface impact strength in a molded article of an impact-resistant styrene resin composition and to improve a balance between the surface impact strength and the rigidity.

[0005] The present inventors have intensively researched to achieve the above objects and have found that, when using a styrene resin composition comprising a styrene copolymer (A), and a block copolymer (B) comprising a polymer block (b1) of a styrene monomer and a polymer block (b2) of a conjugated diene monomer, wherein the styrene copolymer (A) is a ternary copolymer of a styrene monomer (a), a butyl acrylate (b) and a methyl methacrylate (c), the block copolymer (B) can have a predetermined

morphology in the composition, and the styrene resin composition has 9 to 25%, on a weight basis, of structural units derived from the conjugated diene monomer, the resulting molded article exhibits excellent rigidity and remarkably improved surface impact strength, and thus the present invention has been completed.

[0006] The present invention is directed to a styrene resin composition comprising a styrene copolymer (A), and a block copolymer (B) comprising a polymer block (b1) of a styrene monomer and a polymer block (b2) of a conjugated diene monomer, wherein

[0007] the styrene copolymer (A) is a copolymer of a styrene monomer (a), a butyl acrylate (b) and a methyl methacrylate (c),

[0008] the block copolymer (B) has an alternative multi-layered structure comprising the polymer block (b1) and a layer of the polymer block (b2) of the diene monomer are alternately laminated, and

[0009] the styrene resin composition has 9 to 25%, on a weight basis, of structural units derived from the conjugated diene monomer, based on the total amount of the styrene resin composition.

[0010] The present invention is also directed to a forming sheet made of the styrene resin composition.

[0011] The present invention is also directed to a blister pack made of the styrene resin composition.

### BRIEF DESCRIPTION OF DRAWINGS

[0012] FIG. 1 is a transmission electron micrograph (TEM) of a styrene resin composition obtained in Example 3.

[0013] FIG. 2 is a transmission electron micrograph (TEM) of a styrene resin composition obtained in Comparative Example 2.

[0014] FIG. 3 is a flow chart showing an example of a continuous bulk polymerization line having incorporated tubular reactors with mixing elements.

### BEST MODE FOR CARRYING OUT THE INVENTION

[0015] As described above, the transparent styrene resin of the present invention comprises a styrene copolymer (A), and a block copolymer (B) comprising a polymer block (b1) of a styrene monomer and a polymer block (b2) of a conjugated diene monomer, and the styrene copolymer (A) is composed of a styrene monomer (a), a butyl acrylate (b) and a methyl methacrylate (c). The block copolymer (B) has an alternative multi-layered structure in which a layer of the polymer block (b1) and a layer of the polymer block (b2) of the diene monomer are laminated alternatively. The styrene copolymer (A) is provided between layers comprised in the alternative multi-layered structure such that it penetrates into the layers of the multi-layered structure to form a continuous layer. Herein, morphology wherein the styrene copolymer (A) forms the continuous layer and the block copolymer (B) forms the alternative multi-layered structure can be specifically confirmed by a transmission electron micrograph (TEM) shown in FIG. 1. In FIG. 1, the dark portion corresponds to the layer of the polymer block (b2) of the

conjugated diene monomer in the block copolymer (B), while the void portion surrounded by the layer corresponds to the layer of the polymer block (b1) of the styrene monomer.

[0016] The block copolymer (B) composed of the polymer block (b1) of the styrene monomer and the polymer block (b2) of the conjugated diene monomer itself has an alternative multi-layered structure comprising the polymer block (b1) in the block copolymer (B) and the layer of the polymer block (b2) of the conjugated diene monomer. In the present invention, it is made possible to improve the surface impact strength by allowing the styrene copolymer (A) to exist as a continuous layer between layers of a plurality of layers of the polymer block (b2) of the conjugated diene monomer, minimizing the breakage of the alternative multi-layered structure. In contrast, in the case of the prior art wherein SBS is used as a block copolymer and a copolymer of a styrene monomer and a butyl acrylate is used as a continuous layer, since the copolymer is easily compatible with the block copolymer, the morphology of SBS is broken, thereby the surface impact strength of the above-described molded article, especially the surface impact strength of the molded article obtained by secondarily forming a forming sheet, results in an insufficient level.

[0017] In the present invention, it is made possible to exhibit the proper morphology described above in order to achieve a good balance between the surface impact strength and the rigidity by using the methyl methacrylate (c) as the monomer component of the styrene copolymer (A) constituting the continuous layer and controlling the content of structural units derived from the conjugated diene monomer in the styrene resin composition within a range from 9 to 25% on a weight basis. As used herein, the structural units derived from the conjugated diene monomer refer to alkylene structural units obtained by the addition reaction of the conjugated diene monomer. For example, when using 1,3-butadiene as the conjugated diene monomer, the structural units represent but-2-ene-1,4-diyl and but-3-ene-1,2-diyl.

[0018] To form such a proper morphology, the content of structural units derived from the methyl methacrylate (c) in the styrene resin composition is preferably controlled within a range from 1.5 to 6% on a weight basis. As used herein, the structural units derived from the methyl methacrylate (c) refer to structural units obtained by the addition reaction of the methyl methacrylate (c) and are specifically 1-methyl-1-methyloxycarbonyl-ethylene.

[0019] The content of structural units derived from the butyl acrylate (b) also exerts an influence on formation of the morphology of the styrene resin composition and the proportion of the multi-layered structure tends to decrease as the content of the structural units increases. Although the proportion of the multi-layered structure tends to increase as the content of the structural units decreases, the rigidity deteriorates. For the above reason, the content of structural units derived from the butyl acrylate (b) in the styrene resin composition is preferably controlled within a range from 2.8 to 8.5% on a weight basis. As used herein, the structural units derived from the butyl acrylate (b) refers to structural units obtained by the addition reaction of the butyl acrylate (b) and are specifically 1-butyloxycarbonyl-ethylene.

[0020] The contents of the structural units derived from the conjugated diene monomer, the structural units derived

from the methyl methacrylate (c) and the structural units derived from the butyl acrylate (b) in the styrene resin composition can be determined from an area ratio of a chemical peak corresponding to carbon atoms which are peculiar to the respective structural units in the measurement of  $C^{13}$ -NMR. For example, in the case of the structural units derived from the methyl methacrylate (b), the content of the structural units can be determined from an area ratio of a peak of a chemical shift (175 ppm) of carbonyl carbon atoms. In the case of the structural units derived from the butyl acrylate (b), the content of the structural units can be determined from an area ratio of a peak of a chemical shift (63 ppm) of carbon atoms of a butyl group bonded with oxygen atoms.

[0021] In a transparent styrene resin composition of the present invention, the styrene copolymer (A) constituting the continuous layer is a copolymer of the styrene monomer (a), the butyl acrylate (b) and the methyl methacrylate (c). As described above, flexibility can be imparted to the composition by using the butyl acrylate (b) as the copolymer component of the styrene monomer (a) and compatibilization with the styrene-butadiene block copolymer (B), and also morphology of the block copolymer (B) can be retained by using the methyl methacrylate (c).

[0022] Examples of the styrene monomer constituting the styrene copolymer (A) include styrene,  $\alpha$ -methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, ethylstyrene, isobutylstyrene, t-butylstyrene, o-bromostyrene, m-bromostyrene, p-bromostyrene, o-chlorostyrene, m-chlorostyrene, and p-chlorostyrene. Among these styrene monomers, styrene is preferable because it has good reactivity and is easily polymerized.

[0023] The copolymer (A) is preferably a copolymer comprising 78 to 85% by weight of a styrene monomer (a), 6 to 19% by weight of a butyl acrylate (b), and 3 to 16% by weight of a methyl methacrylate (c), based on the total amount of the copolymer (A). As described hereinafter, the content of the polybutadiene block in the block copolymer (B) is preferably from 20 to 30% by weight in view of the surface impact strength of the molded article, based on the total amount of the block copolymer (B). By controlling the proportion of the raw monomer of the styrene copolymer (A) within the above range of 78 to 85% by weight, excellent transparency can be imparted to the molded article, and in addition, good balance between the surface impact strength and the rigidity is achieved. It is particularly preferable, in view of the transparency of the molded article, to control the proportion of the monomer so as to reduce a difference in refractive index between the styrene copolymer and the block copolymer (B) to 0.002 or less. By using the methyl methacrylate (c) in the above proportion of 3 to 16% by weight, excellent heat resistance can be imparted to the molded article, and thus excellent rigidity and excellent surface impact strength can be exhibited in use in high-temperature area and use in the summer. Furthermore, by using the methyl methacrylate (c) in the above proportion, proper fluidity is exhibited upon melting while maintaining the molecular weight of the styrene copolymer (A) at a relatively low value, thereby making it possible to exhibit good molding ability. Therefore, the resulting continuous layer made of the styrene copolymer (A) has proper flexibility and thus whitening on bending of the forming sheet can be prevented. From such a point of view, the styrene

copolymer (A) is preferably a styrene copolymer having a weight average molecular weight of  $25 \times 10^4$  to  $35 \times 10^4$ , and a melt mass flow rate is preferably from 5 to 12 g/10 min. As described above, since the styrene copolymer (A) can exhibit proper fluidity while maintaining the molecular weight at a low value, the temperature upon melt-kneading of the styrene copolymer (A) and the block copolymer (B) can be reduced. As a result, gelation upon melt-kneading can be prevented from occurring and the finally obtained molded article has excellent appearance.

[0024] Such a styrene copolymer (A) can be produced by polymerizing the styrene monomer (a), the butyl acrylate (b), and the methyl methacrylate (c) in a predetermined weight ratio. Examples of the polymerization method are a suspension polymerization method, a bulk suspension polymerization method, a solution polymerization method, and a bulk polymerization method; however, a continuous bulk polymerization method is preferable in view of productivity, cost, and uniformity of the composition.

[0025] In the present invention, among the continuous bulk polymerization methods, particularly preferred is a continuous bulk polymerization method using a polymerization apparatus comprising a polymerization line in which plural tubular reactors with static mixing elements are incorporated in series because the homogeneous styrene copolymer (A) can be efficiently produced.

[0026] The mixing elements used herein include, for example, those that divide the polymerization solution that has flowed into the tube, and change the direction of its flow and repeat such a division and combination to mix the polymerization solution. Such a tubular reactor includes, for example, SMX model and SMR model Sulzer tubular mixers, Koenigs static mixers, Toray tubular mixers, etc.

[0027] According to the continuous bulk polymerization method, raw components are preferably prepolymerized in the stirring type reactor before introduction into the polymerization apparatus, and then the polymerization liquid is continuously introduced in the polymerization apparatus constituting the continuous bulk polymerization line because uniformity of the styrene copolymer (A) is further enhanced. The stirring type reactor includes, for example, a stirring tank reactor, a stirring tower reactor, etc., and the stirring blade includes, for example, anchor type, turbine type, screw type, double helical type, and logborn type blades. In the case in which the respective raw components are polymerized in the continuous polymerization line comprising the stirring type reactor connected to the continuous bulk polymerization apparatus, the temperature is preferably from 120 to 135° C. at a polymerization initial stage where a polymerization conversion ratio is from 35 to 55% by weight, or the temperature is preferably from 140 to 160° C. at the subsequent polymerization stage. When the above temperature conditions are satisfied, the molecular weight of the resulting styrene copolymer (A) can be easily controlled, and the productivity can be improved.

[0028] After the completion of the polymerization, the polymerization solution is preheated in a preheater and is sent to a devolatilizing bath and, after removing the unreacted monomer and solvent under reduced pressure, the polymerization solution is pelletized to obtain the desired styrene copolymer (A).

[0029] In the continuous bulk polymerization method, a solvent may be used so as to reduce the viscosity of the

polymerization solution in the tubular reactor. In this case, the amount of the solvent is within a range from 5 to 20 parts by weight based on 100 parts by weight of the total of the respective raw components. For example, ethylbenzene, toluene and xylene, which are used in the bulk polymerization method, are suitable for use as the solvent. A chain transfer agent is preferably added so as to adjust the molecular weight of the styrene copolymer (A). The amount of the chain transfer agent is usually within a range from 0.005 to 0.5 parts by weight based on 100 parts by weight of the total of the respective raw monomers.

[0030] In the production of the styrene copolymer (A), a polymerization initiator can be appropriately used. As the polymerization initiator, any conventional peroxide-based polymerization initiators can be used. In the present invention, among known peroxide polymerization initiators, 2,2-bis(4,4-di-*t*-butylperoxycyclohexyl)propane is preferable because the styrene copolymer (A) can be three-dimensionally polymerized and a neck-in phenomenon upon extrusion of the sheet can be prevented.

[0031] Examples of the block copolymer (B) composed of a polymer block (b1) of a styrene monomer and a polymer block (b2) of a conjugated diene monomer include:

[0032] (1) a diblock copolymer comprising a polymer block (b1) of a styrene monomer and a polymer block (b2) of a conjugated diene monomer,

[0033] (2) a triblock copolymer comprising a polymer block (b1) of a styrene monomer and a polymer block (b2) of a conjugated diene monomer, and a polymer block (b1) of a styrene monomer,

[0034] (3) a hydrogenated compound of the triblock copolymer,

[0035] (4) a polyblock copolymer consisting of plural polymer blocks higher than triblocks, comprising a polymer block (b1) of plural styrene monomers and a polymer block (b1) of a styrene monomer, and

[0036] (5) a block copolymer comprising a polymer block (b1) of a styrene monomer and a polymer block (b2) of a conjugated diene monomer, and a block copolymer having a random copolymer moiety.

[0037] Among these copolymers, the triblock copolymer (2) is preferable because it is morphologically excellent in surface impact resistance of the rubbery polymer (B). With respect to the triblock copolymer, the conjugated diene monomer may be partially copolymerized with the polymer block (b1) of the styrene monomer, or the styrene monomer may be partially copolymerized with the polymer block (b2) of the conjugated diene monomer.

[0038] Examples of the styrene monomer constituting the polymer block (b1) include styrene,  $\alpha$ -methylstyrene, *o*-methylstyrene, *m*-methylstyrene, *p*-methylstyrene, ethylstyrene, isobutylstyrene, *t*-butylstyrene, *o*-bromostyrene, *m*-bromostyrene, *p*-bromostyrene, *o*-chlorostyrene, *m*-chlorostyrene, and *p*-chlorostyrene. In the present invention, styrene is preferable because the above alternately laminated state is easily formed.

[0039] Examples of the conjugated diene monomer constituting the polymer block (b2) include diene monomers such as butadiene, chloroprene, isoprene, and 1,3-pentadi-

ene. Among these monomers, a polybutadiene block copolymer is preferable because it is excellent in rubber elasticity exhibited by the polymer block (b2) and excellent surface impact strength can be imparted to the finally obtained styrene resin composition of the present invention.

[0040] Therefore, the block copolymer (B) is preferably a so-called styrene-butadiene copolymer (SBR) or a triblock type styrene-butadiene-styrene copolymer (SBS), and the styrene-butadiene-styrene copolymer (SBS) is particularly preferable in view of surface impact strength.

[0041] When the content of the polymer block (b2) of the conjugated diene monomer in the block copolymer (B) increases, the block copolymer (B) has enhanced rubbery properties and plastic deformation hardly arises upon processing. Therefore, the content of the polymer block (b2) of the conjugated diene monomer in the block copolymer (B) is preferably from 20 to 30% by weight.

[0042] The block copolymer (B) described in detail above can be produced by polymerizing a styrene monomer with a conjugated diene monomer using a known method such as emulsion polymerization or solution polymerization method. The triblock copolymer is preferably produced by a method of solution-polymerizing a styrene monomer with a diene monomer in a hydrocarbon organic solvent in the presence of an anionic polymerization initiator such as organolithium compound because the molecular weight of the block copolymer (B) can be easily increased.

[0043] The styrene resin composition of the present invention can be obtained by melt-kneading the styrene copolymer (A) with the block copolymer (B). In the present invention, by melt-kneading the two, it is made possible to allow the styrene copolymer (A) to exist as a continuous layer between layers of the polymer block (b1) of the styrene monomer and layers of the polymer block (b2) of the conjugated diene monomer, which are alternately laminated, without breaking the morphology of the block copolymer (B).

[0044] In this case, as described above, a mixing ratio of the styrene copolymer (A) to the block copolymer (B) is controlled so that the content of the structural units derived from the conjugated diene monomer, as raw components of the block copolymer (B), in the styrene resin composition is from 9 to 25% by weight. When the content of the structural units derived from the conjugated diene monomer in the styrene resin composition of the present invention is less than 9% by weight, sufficient surface impact strength cannot be imparted to the molded article. On the other hand, when the content exceeds 25% by weight, the composition itself has insufficient rigidity and drawdown is likely to occur when secondarily forming the forming sheet. The content is particularly preferably within a range from 14 to 25% by weight because a remarkable effect of improving the surface impact strength is exerted. The styrene copolymer (A) is preferably mixed with the block copolymer (B) so that the content of the structural units derived from the methyl methacrylate (c) in the styrene resin composition is within a range from 1.5 to 6% by weight and the content of the structural units derived from the butyl acrylate (b) in the styrene resin composition is within a range from 2.8 to 9.5% by weight.

[0045] As used herein, the structural units derived from the conjugated diene monomer refer to alkylene structural

units obtained by the addition reaction of the conjugated diene monomer. For example, when using 1,3-butadiene as the conjugated diene monomer, the structural units represent but-2-ene-1,4-diyl and but-3-ene-1,2-diyl. Also the content of the structural units in the styrene resin composition can be determined from an area ratio of a chemical peak corresponding to carbon atoms which are peculiar to the respective structural units in the measurement of  $C^{13}$ -NMR. The content can be determined from an area ratio of a peak of a chemical shift (114 ppm) of terminal carbon atoms constituting a 1,2-vinyl group in the case of but-3-ene-1,2-diyl, and the content can be determined from an area ratio of a peak of a chemical shift (125 to 132 ppm) of terminal carbon atoms in the case of but-2-ene-1,4-diyl.

[0046] Specific method of melt-kneading the styrene copolymer (A) with the block copolymer (B) includes, for example, a method of uniformly dry-blending the two using a mixer, charging the mixture in an extruder and melt-kneading the mixture, and a method of charging the styrene copolymer (A) and the block copolymer (B) in an extruder and melt-kneading them.

[0047] For example, there can also be used a method of previously dry-blending pellets or pearls of the styrene copolymer (A) and the block copolymer (B) using a mixer such as a Banbury mixer, charging the resulting mixture in an extruder, or directly charging the pellets or pearls in the extruder, and melt-kneading them in the extruder at 190 to 240° C. The melt-kneaded mixture may be formed into a sheet, or the mixture may be once pelletized and the resulting pellets be melt-formed into a sheet using an extruder. Melt-kneading is conducted using a single screw kneader, a twin screw kneader, a kneader, or an open roller. The resin temperature upon extrusion is preferably a melting temperature of the styrene copolymer (A) and the block copolymer (B) and is lower than 210° C. in order to inhibit formation of a gel and to improve the appearance of the molded article at the same.

[0048] In the present invention, in the case of polymerizing the respective raw components to obtain the styrene copolymer (A) and the block copolymer (B), or in the case of melt-kneading the two, various additives such as antioxidants, releasants, ultraviolet absorbers, colorants, heat stabilizers, plasticizers, and dyes can be appropriately added. These additives can be added during kneading or polymerization of the respective polymers. Specific examples of the additive include plasticizers such as mineral oil, ester-based plasticizer and polyester-based plasticizer, antioxidants, chain transfer agents, higher fatty acids, high fatty acid esters, metal salts of higher fatty acids, and silicone oil, and one or more kinds thereof can be used in combination.

[0049] In the present invention, for the purpose of further improving the surface impact strength, it is made possible to add a block copolymer comprising a polymer block of a styrene monomer having 50% by weight or less of structural units derived from the styrene monomer, and a polymer block of a conjugated diene monomer in the styrene resin composition in the proportion of 2 to 15% by weight.

[0050] Examples of the method of producing a forming sheet from the styrene resin composition of the present invention includes, for example, a method of melt-kneading the styrene copolymer (A) with the block copolymer (B) and extruding the mixture through a T-die, and a method of

forming a film by a calendering method or an inflation extrusion method. As described above, there can be produced a sheet having a thickness of 0.02 to 3 mm, and preferably 0.03 to 1 mm, which is suitable for secondary forming.

[0051] The forming sheet thus obtained is excellent in transparency, surface impact strength, rigidity, resistance to whitening on bending, and formability. Regarding the transparency, a 0.4 mm thick sheet exhibits a Haze value of 5 or less according to JIS K7105. Regarding the surface impact strength, a 0.4 mm thick sheet exhibits a DuPont impact strength of 0.8 J or higher, which has not previously been achieved. The heat resistance of the molded article is improved, and thus no deformation occurs under the conditions of high temperature and high humidity (after standing at a temperature of 65° C. and a humidity of 80% for 8 hours).

[0052] In the present invention, the forming sheet can be further formed into a desired shape by a pressure molding or a heat-pressure molding technique. The forming sheet is suitable for use as blister packs, trays for packing foods, cover materials, cups, various trays for storage, carrier tapes, and shrink films because it is excellent in resistance to whitening on bending, and has a balance between the surface impact strength, and rigidity. In particular, the forming sheet is suitable for use as blister packs because it is excellent in resistance to whitening on bending, and has heat resistance.

[0053] The styrene resin composition of the present invention can also be applied to shrink films. The shrink film can be produced by melt-kneading the styrene resin composition of the present invention, extruding the kneaded mixture and monoaxially stretching the extrudate.

[0054] The stretching method in the production of the shrink film is not specifically limited, and there can be preferably used a method of monoaxially or biaxially stretching, simultaneously or successively.

[0055] In the case of flat-shaped monoaxial stretching, there can be used a method of stretching in an extrusion direction by means of a difference in speed between heat rollers, or a method of independently stretching in a direction perpendicular to the extrusion direction using a tenter. In the case of biaxial stretching, there can be used a method of longitudinally stretching in an extrusion direction by means of a difference in speed between heat rolls and stretching in a lateral direction using a tenter, or a method of simultaneously stretching in lateral and longitudinal directions in a tenter.

[0056] In the case of cyclic monoaxial stretching, there can be used a method of stretching in an extrusion direction while inhibiting expansion of bubbles in a section diameter direction and controlling a draft ratio. In the case of cyclic biaxial stretching, there can be used a method of stretching in an extrusion direction and stretching simultaneously or successively in a section diameter direction of bubbles while blowing air into the bubbles of the cylindrically extruded sheet.

[0057] Since the transparent styrene resin composition of the present invention has excellent rigidity, surface impact resistance, moldability and transparency, it can be applied to various uses for moldings such as injection molding, contour extrusion molding, vacuum molding and pressure molding,

in addition to uses such as sheet and shrink film, and also can be used as housings and parts of household electric appliances, various parts of office automation equipment, stationery articles, and general merchandise.

## EXAMPLES

[0058] The present invention will be described in detail by way of the following examples; however, the present invention is not limited thereto. In the examples, parts and percentages are by weight unless otherwise specified.

### [Production of Styrene Copolymer (A)]

[0059] In the production of a styrene copolymer (A), a continuous polymerization apparatus is equipped with a polymerization line as shown in the flow chart in FIG. 3. The polymerization apparatus is composed of a plunger pump (1), a stirring type reactor (2), gear pumps (3), (7) and (11), and tubular reactors (4), (5), (6), (8), (9) and (10), each having therein a mixing element. In FIG. 3, the arrow indicates the direction of liquid flow of a polymerization liquid and raw components are sent by the plunger pump (1) to the stirring type reactor (2), are subjected to initial graft polymerization while stirring, are introduced into a circulation polymerization line (I) composed of the tubular reactors (4), (5), (6) and the gear pump (7) by the gear pump (3), and then the polymerization liquid is polymerized in the circulation polymerization line (I) while circulating. The tubular reactors (8), (9) and (10) and the gear pump (11) forms a non-circulation polymerization line (II), and a portion of the polymerization liquid in the circulation line (I) flows into the polymerization line (II) and is then polymerized to the desired polymerization degree in the polymerization line (II).

[0060] The polymerization in the circulation polymerization line (I) is conducted until the total polymerization conversion ratio of the styrene monomer (a), the butyl acrylate (b) and the methyl methacrylate (c) at an outlet of the circulation polymerization line (I) becomes 35 to 55% by weight, and preferably 40 to 50% by weight. A ratio of a flow rate of the polymerization liquid circulation in the circulation polymerization line (I) to a flow rate of the polymerization liquid which flows into the non-circulation polymerization line (II), a reflux ratio  $R (=F1/F2)$ , where  $F1$  denotes a flow rate (liter/hour) of the mixed solution refluxed in the circulation polymerization line (I) without flowing into the polymerization line (II), and  $F2$  denotes a flow rate (liter/hour) of the mixed solution which flows into the non-circulation polymerization line (II) from the circulation polymerization line (I) is usually controlled within a range from 3 to 15.

[0061] After the completion of the polymerization, the polymerization solution is sent to a preheater by the gear pump (11), then to a devolatilizing bath and, after removing the unreacted monomer and the solvent under reduced pressure, the polymerization solution is pelletized to obtain the desired styrene copolymer (A).

### (Production of Styrene Copolymer (A-1))

[0062] A mixed solution of 82 parts of styrene (SM), 12 parts of butyl acrylate (BuA), 6 parts of methyl methacrylate (MMA) and 8 parts of ethylbenzene was prepared and, after adding 2,2-bis(4,4-di-peroxycyclohexyl)propane, as a polymerization initiator, in an amount of 0.025 parts based on

100 parts of the monomer mixture and n-dodecylmercaptane, as a chain transfer agent, in an amount of 0.01 parts based on 100 parts of the monomer mixture, the solution was continuously bulk-polymerized under the following conditions using the above polymerization apparatus.

[0063] Reaction temperature in the stirring type reactor (2): 115° C.

[0064] Reaction temperature in the circulation polymerization line (I): 132° C.

[0065] Reaction temperature in the polymerization line (II): 150° C.

[0066] The mixed solution obtained by the polymerization was heated to 215° C. by a heat exchanger and, after removing the volatile component under reduced pressure, the polymerization solution was pelletized to obtain the desired styrene copolymer (A-1). Physical properties of the resulting styrene copolymer are shown in Table 1.

(Production of Styrene Copolymer (A-2))

[0067] In the same manner as in the case of the production of the styrene copolymer (A-1), except for adding 2,2-bis(4,4-di-peroxycyclohexyl)propane, as a polymerization initiator, in an amount of 0.025 parts based on 100 parts of the monomer mixture and n-dodecylmercaptane, as a chain transfer agent, in an amount of 0.02 parts based on 100 parts of the monomer mixture to a mixed solution of 82 parts of styrene (SM), 12 parts of butyl acrylate (BuA), 6 parts of methyl methacrylate (MMA) and 9 parts of ethylbenzene, a styrene copolymer (A-2) was obtained. Physical properties of the resulting styrene copolymer are shown in Table 1.

(Production of Styrene Copolymer (A-3))

[0068] In the same manner as in the case of the production of the styrene copolymer (A-1), except for adding 2,2-bis(4,4-di-peroxycyclohexyl)propane, as a polymerization initiator, in an amount of 0.025 parts based on 100 parts of the monomer mixture and n-dodecylmercaptane, as a chain transfer agent, in an amount of 0.03 parts based on 100 parts of the monomer mixture to a mixed solution of 82 parts of styrene (SM), 8 parts of butyl acrylate (BuA), 10 parts of methyl methacrylate (MMA) and 9 parts of ethylbenzene, a styrene copolymer (A-3) was obtained. Physical properties of the resulting styrene copolymer are shown in Table 1.

(Production of Styrene Copolymer (A-4))

[0069] A mixed solution of 82 parts of styrene (SM), 5 parts of butyl acrylate (BuA), 13 parts of methyl methacrylate (MMA) and 6 parts of ethylbenzene was prepared and, after adding t-butylperoxyisopropyl monocarbonate, as a polymerization initiator, in an amount of 0.025 parts based on 100 parts of the monomer mixture and n-dodecylmercaptane, as a chain transfer agent, in an amount of 0.03 parts based on 100 parts of the monomer mixture, the solution was continuously bulk-polymerized under the following conditions using the polymerization line shown in the flow chart in FIG. 3.

[0070] Reaction temperature in the stirring type reactor (2): 119° C.

[0071] Reaction temperature in the circulation polymerization line (I): 124° C.

[0072] Reaction temperature in the polymerization line (II): 150° C.

[0073] The mixed solution obtained by the polymerization was heated to 215° C. by a heat exchanger and, after removing the volatile component under reduced pressure, the polymerization solution was pelletized to obtain the desired styrene copolymer (A-4). Physical properties of the resulting styrene copolymer are shown in Table 1.

(Production of Styrene Copolymer (A-5))

[0074] In the same manner as in the case of the production of the styrene copolymer (A-1), except for adding 2,2-bis(4,4-di-peroxycyclohexyl)propane, as a polymerization initiator, in an amount of 0.025 parts based on 100 parts of the monomer mixture and n-dodecylmercaptane, as a chain transfer agent, in an amount of 0.03 parts based on 100 parts of the monomer mixture to a mixed solution of 82 parts of styrene (SM), 5 parts of butyl acrylate (BuA), 13 parts of methyl methacrylate (MMA) and 9 parts of ethylbenzene, a styrene copolymer (A-5) was obtained. Physical properties of the resulting styrene copolymer are shown in Table 1.

(Production of styrene copolymer (A-6))

[0075] A mixed solution of 82 parts of styrene (SM), 18 parts of butyl acrylate (BuA) and 9 parts of ethylbenzene was prepared and, after adding 2,2-bis(4,4-di-peroxycyclohexyl)propane, as a polymerization initiator, in an amount of 0.026 parts based on 100 parts of the monomer mixture, the solution was continuously bulk-polymerized under the following conditions using the polymerization line shown in the flow chart in FIG. 3.

[0076] Reaction temperature in the stirring type reactor (2): 115° C.

[0077] Reaction temperature in the circulation polymerization line (I): 132° C.

[0078] Reaction temperature in the polymerization line (II): 150° C.

[0079] The mixed solution obtained by the polymerization was heated to 215° C. by a heat exchanger and, after removing the volatile component under reduced pressure, the polymerization solution was pelletized to obtain the desired styrene copolymer (A-6). Physical properties of the resulting styrene copolymer are shown in Table 1.

[Production of Styrene Resin Compositions and Evaluation of Physical Properties]

(Styrene-butadiene-styrene Block Copolymer (B))

[0080] The styrene-butadiene-styrene block copolymers (B) used in the following respective examples and comparative examples are as follows.

[0081] Styrene-butadiene-styrene block copolymer (B1):

[0082] SBS manufactured by Chevron Phillips Chemical Company under the trade name of "K Resin KR05"

[0083] Content of a constituent unit derived from styrene: 75% by weight

[0084] Content of a constituent unit derived from butadiene: 25% by weight

[0085] MFR: 7 g/10 min



[0086] Styrene-butadiene-styrene block copolymer (B2):

[0087] SBS manufactured by Chevron Phillips Chemical Company under the trade name of "K Resin DK11"

[0088] Content of a constituent unit derived from styrene: 75% by weight

[0089] Content of a constituent unit derived from butadiene: 25% by weight

[0090] MFR: 8 g/10 min

[0091] Hereinafter, the styrene-butadiene-styrene block copolymers (B1) and (B2) are abbreviated to as a "block copolymer (B1)" and a "block copolymer (B2)", respectively.

(Measurement by  $C^{13}$ -NMR)

[0092] The contents of structural units derived from a conjugated diene monomer, structural units derived from a methyl methacrylate (c) and structural units derived from a butyl acrylate (b) in the styrene resin compositions obtained in the respective examples and comparative examples were measured in the following manner.

[0093] 120 mg of each of samples obtained in the respective examples and comparative examples was dissolved in 0.5 ml of  $CDCl_3$ , mixed with about 5 mg of a relaxation agent, and then filled in a sample tube for measurement of NMR. Using NMR "GSX-400" manufactured by JEOL Ltd., quantitative  $^{13}C$ -NMR was performed by a gate-coupling method.

[0094] The content of each structural unit was determined from an area ratio of a chemical peak of the following carbon atoms.

[0095] Carbon atoms as a measuring object and chemical shift corresponding thereto

[0096] Aromatic carbon atoms in the case of the structural units derived from styrene: 142 to 146 ppm

[0097] Carbonyl carbon atoms in the case of the structural units derived from methyl methacrylate: 175 ppm

[0098] Carbon atoms of a butyl group bonded with oxygen atoms in the case of the structural units derived from butyl acrylate: 63 ppm

[0099] Terminal carbon atoms constituting a 1,2-vinyl group in the case of structural units (but-3-ene-1,2-diyl) derived from butadiene: 114 ppm

[0100] Terminal carbon atoms in the case of structural units (but-2-ene-1,4-diyl) derived from butadiene: 125 to 132 ppm

[Method for Evaluation of Physical Properties]

[0101] Methods for evaluation of physical properties of the forming sheets in the following respective examples and comparative examples are as follows.

(Measurement of Haze)

[0102] According to JIS K7105, a Haze value, which indicates transparency of a 0.4 mm thick sheet test piece, was measured by a HAZE TURBIDIMETER (manufactured by Nippon Denshoku Industries Co., Ltd.).

(Measurement of DuPont Impact Strength)

[0103] Using a DuPont impact tester (manufactured by Toyo Seiki Seisaku-Sho, Ltd.), energy at 50% breaking of a 0.4 mm thick sheet test piece was measured under the conditions of a weight of 300 g, an impact head radius of 6.3 mm and a bearer radius of 6.3 mm.

(Measurement of Tensile Elasticity)

[0104] According to JIS K7161, tensile elasticity was measured at a test speed of 1 mm/min.

(Measurement of Melt Weight Flow Rate)

[0105] According to JIS K7210, a melt weight flow rate was measured at a temperature of 200° C. under a load of 5 Kgf.

(Test of Whitening on Bending)

[0106] A 0.4 mm thick sheet was bent by 180° and returned to an original state, and then the width of the whitened portion was measured by a caliper.

(Evaluation of Appearance of Sheet)

[0107] ○: extruded sheet has no appearance defects such as fisheyes, hard spots, or sharkskin

[0108] x: extruded sheet has appearance defects such as fisheyes, hard spots, or sharkskin

(Evaluation of Heat Resistance)

[0109] A 0.4 mm thick sheet was molded into a box measuring 170×130×35 (mm) by a vacuum molding machine and the resulting molded article was left to stand in a constant-temperature bath at a temperature of 65° C. and a humidity of 80% for 8 hours, and then deformation of the molded article was confirmed.

[0110] ○: molded article with no deformation

[0111] X: molded article with some deformation

(Measurement of Neck-in)

[0112] After measuring the width (W) of the extruded sheet, neck-in was calculated by the following equation:

$$\text{Neck-in (mm)} = W_0 - W$$

where  $W_0$  denotes a die width.

Example 1

[0113] A styrene copolymer (A-1) was mixed with a styrene-butadiene-styrene block copolymer (B1) in a proportion of (A-1)/(B1)=50/50 on a weight basis, and then the mixture was extruded to form a 0.4 mm thick sheet.

[0114] Using the resulting sheet, various physical properties were evaluated. The results are shown in Table 3. The molding conditions of the sheet were as follows.

[0115] Sheet forming machine: 30 mm extruder, Model UEV, manufactured by Union Plastic Co., Ltd.

[0116] Cylinder temperature: 210° C.

[0117] T-die set temperature: 210° C.

[0118] T-die lip width: 200 mm

[0119] Take-up speed: 1 m/min

[0120] Screw speed: 65 rpm

## Example 2

[0121] A styrene copolymer (A-1) was mixed with a block copolymer (B2) in a proportion of (A-1)/(B2)=40/60 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 2.

## Example 3

[0122] A styrene copolymer (A-1) was mixed with a block copolymer (B2) in a proportion of (A-1)/(B2)=40/60, and then the mixture was extruded to form a 0.4 mm thick sheet on the extrusion conditions below, and various physical properties were evaluated. The results are shown in Table 2.

[0123] Sheet forming machine: 120 mm extruder manufactured by Hitachi Zosen Sangyo Co., Ltd.

[0124] Cylinder temperature: 210° C.

[0125] T-die set temperature: 210° C.

[0126] T-die lip width: 1030 mm

[0127] Take-up speed: 22 m/min

[0128] Screw speed: 60 rpm

[0129] In addition, after cutting out a portion of the sheet and staining with osmium tetroxide, an ultra-thin section was made from the cross section in the direction of CD using an ultramicrotome, and then a transmission electron micrograph (TEM) was taken. The resulting transmission electron micrograph is shown in FIG. 1.

## Example 4

[0130] A styrene copolymer (A-1) was mixed with a block copolymer (B2) in a proportion of (A-1)/(B2)=30/70 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 2.

## Example 5

[0131] A styrene copolymer (A-2) was mixed with a block copolymer (B1) in a proportion of (A-3)/(B1)=50/50 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 2.

## Example 6

[0132] A styrene copolymer (A-3) was mixed with a block copolymer (B1) in a proportion of (A-4)/(B1)=50/50 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 2.

## Example 7

[0133] A styrene copolymer (A-1) was mixed with a block copolymer (B1) and a styrene-butadiene block copolymer elastomer ("TR2003", manufactured by JSR Co.) having 43% by weight of styrene monomer constituent units and 57% by weight of butadiene monomer structural units in a

proportion of (A-1)/(B1)/(TR2003)=40/50/10 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 2.

## Example 8

[0134] A styrene copolymer (A-4) was mixed with a block copolymer (B1) in a proportion of (A-4)/(B1)=50/50 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 2.

## Example 9

[0135] A styrene copolymer (A-5) was mixed with a block copolymer (B1) in a proportion of (A-5)/(B1)=50/50 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 2.

## Example 10

[0136] A styrene copolymer (A-1) was mixed with a block copolymer (B1) in a proportion of (A-5)/(B1)=40/60 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 2.

## Comparative Example 1

[0137] A styrene copolymer (A-6) was mixed with a block copolymer (B1) in a proportion of (A-6)/(B1)=40/60 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 3.

## Comparative Example 2

[0138] A styrene copolymer (A-6) was mixed with a block copolymer (B2) in a proportion of (A-6)/(B1)=40/60 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 3.

[0139] After cutting out a portion of the resulting sheet and staining with osmium tetroxide, an ultra-thin section was made from the cross section in the direction of CD using an ultramicrotome, and then a transmission electron micrograph (TEM) was taken. The resulting transmission electron micrograph is shown in FIG. 2.

## Comparative Example 3

[0140] A styrene copolymer (A-6) was mixed with a block copolymer (B2) in a proportion of (A-6)/(B1)=30/60 on a weight basis, and then a 0.4 mm thick sheet was formed under the same conditions as in Example 1 and various physical properties were evaluated. The results are shown in Table 3.

TABLE 1

	Styrene copolymer					
	A-1	A-2	A-3	A-4	A-5	A-6
(a) Styrene (parts)	82	82	82	87	76	82
(b) BuA (parts)	12	8	12	8	15	18
(c) MMA (parts)	6	10	6	5	9	—
MFR (g/10 min)	8.3	10.2	8.3	8.8	8.2	4.8
Mw $\times 10^4$	26.8	22.3	25.2	25.0	27.0	38.2
Haze of sheet (%)	0.5	0.5	0.5	0.5	0.5	0.5

[0141]

[0144] It is also made possible to avoid poor appearance due to whitening upon bending and impact in a forming sheet and to impart excellent transparency and excellent heat resistance to a secondarily formed article made from the forming sheet. Therefore, the styrene resin composition of the present invention is remarkably suitable for use in blister packs, trays for packing foods, cover materials, cups, various trays for storage, carrier tapes, and shrink films.

1. A styrene resin composition comprising (a) styrene copolymer (A), and a block copolymer (B) comprising a polymer block (b1) of a styrene monomer and a polymer block (b2) of a conjugated diene monomer, wherein

TABLE 2

	Examples									
	1	2	3	4	5	6	7	8	9	10
Copolymer (A-1)	50	40	40	30			40			40
Copolymer (A-2)					50					
Copolymer (A-3)						50				
Copolymer (A-4)								50		
Copolymer (A-5)									50	
Block copolymer (B1)	50				50	50	50	50	50	60
Block copolymer (B2)		60	60	70						
TR2003							10			
Butadiene content %	12.5	15	15	17.5	12.5	12.5	18.2	12.5	12.5	15
MMA content %	3.2	2.6	2.6	2.0	4.2	3.2	2.6	2.7	4.7	2.4
BuA content %	6	4.8	4.8	3.6	4	6	4.8	7.5	7.5	4.8
Haze (%)	2.4	2.34	2.26	3.51	3.2	3.2	3.5	12.0	15.0	3.09
DuPont impact strength (J)	1.3	0.69	0.81	0.98	1.0	0.9	1.52	1.2	1.1	0.92
Tensile elasticity (Mpa)	1590	1740	1570	1460	1620	1550	1480	1650	1560	1470
Whitening on bending	1.3	1.2	1.2	1.1	1.3	1.3	1.0	1.3	1.2	1.2
Appearance of sheet	○	○	○	○	○	○	○	○	○	○
Heat resistance	○	○	○	○	○	○	○	○	○	○
Neck-in (mm)	45	37	—	31	45	51	45	45	45	37

Note:

In the table, "TR2003" is a thermoplastic elastomer "TR2003", manufactured by JSR Co. (styrene-butadiene block copolymer having 43% by weight of styrene monomer constituent units and 57% by weight of butadiene monomer structural units).

[0142]

TABLE 3

	Comparative Examples		
	1	2	3
Copolymer (A-6)	40	40	30
Block copolymer (B1)	60		
Block copolymer (B2)		60	70
Butadiene content %	15	15	17.5
BuA content %	7.2	7.2	5.4
Haze (%)	4.68	4.55	5.61
DuPont impact strength (J)	0.85	0.14	0.29
Tensile elasticity (Mpa)	1530	1810	1530
Whitening on bending	1.1	1.3	1.3
Appearance of sheet	x	x	x
Heat resistance	x	x	x
Neck-in (mm)	37	37	31

## INDUSTRIAL APPLICABILITY

[0143] According to the present invention, it is made possible to remarkably improve surface impact strength in a molded article of a styrene resin composition and to improve the balance between the surface impact strength and the rigidity.

the styrene copolymer (A) is a copolymer of a styrene monomer (a), a butyl acrylate (b) and a methyl methacrylate (c),

the block copolymer (B) has an alternative multi-layered structure comprising a layer of the polymer block (b1) and a layer of the polymer block (b2) of the diene monomer, and

the styrene resin composition has, on a weight basis, 9 to 25%, of structural units derived from the conjugated diene monomer, 2.8 to 9.5% of structural units derived from the butyl acrylate (b), and 1.5 to 6% of structural units derived from the methyl methacrylate (c), based on the total amount of the styrene resin composition.

2-3. (canceled)

4. The styrene resin composition according to claim 1, wherein the styrene copolymer (A) is a copolymer comprising 78 to 85% by weight of a styrene monomer (a), 6 to 19% by weight of a butyl acrylate (b), and 3 to 16% by weight of a methyl methacrylate (c), based on the total amount of the copolymer (A); and the block copolymer (B) contains 20 to 30% by weight of the polymer block (b2) of the conjugated diene monomer in the block copolymer (B), based on the total amount of the block copolymer (B).

5. The styrene resin composition according to claim 4, wherein the styrene copolymer (A) is a styrene copolymer having a weight average molecular weight of  $25 \times 10^4$  to  $35 \times 10^4$ .

6. The styrene resin composition according to claim 1, wherein the block copolymer (B) composed of the polymer block (b1) of the styrene monomer and the polymer block (b2) of the conjugated diene monomer has a weight average

molecular weight of 130,000 to 170,000 and a molecular weight distribution (Mw/Mn) of 1.3 to 1.7.

7. A forming sheet made of the styrene resin composition of claim 1.

8. A blister pack made of the styrene resin composition of claim 1.

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